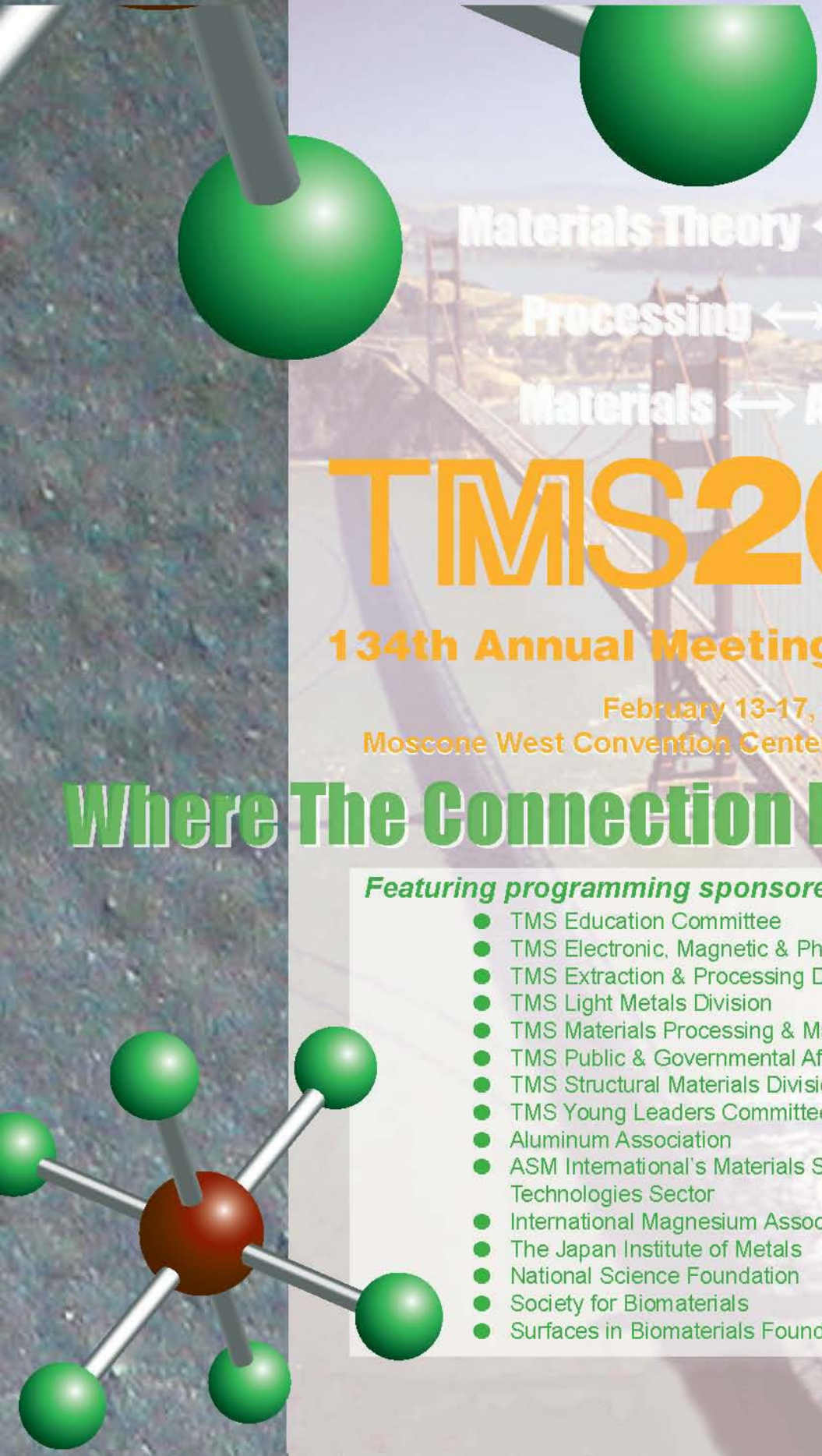

Materials Theory ⟷ Experiment

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TECHNICAL PROGRAM

Moscone West Convention Center; San Francisco, California USA; February 13-17, 2005

MONDAY

Alumina and Bauxite: Industry Trends and Developments

Sponsored by: Light Metals Division, LMD-Aluminum Committee
Program Organizers: Dag Olsen, Hydro Aluminium AS, Porsgrunn 3907 Norway; Travis Galloway, Century Aluminum, Hawesville, KY 42348 USA; Halvor Kvande, Norsk Hydro ASA, Oslo N-0240 Norway

Monday AM Room: 2005
February 14, 2005 Location: Moscone West Convention Center

Session Chair: Victorio Siqueira, CVRD, Alumina Business, Rio de Janeiro, RJ 20030 900 Brazil

8:30 AM
Bauxite Mining Sustainably: *Patrick Riley Atkins*[1]; [1]Alcoa, Inc., 390 Park Ave., New York, NY 10022 USA

Beginning in 1990, The international Aluminum Institute began a program to report on the bauxite mineing and rehabilitation activities of the worldwide industry. A survey process was initiated and reports were published in 1992, 1998 and 2004. The recently published 2004 report includes extensive data on mines that represent over 70% of the world's output of bauxite. This paper describe the latest report and will focus on the mine rehabilitation technologies,progress and performance, on company/community interactions and the sustainability goals of the industry.

8:55 AM
Bauxite Supply to the Aluminum Industry - An Update and New Perspective: *William Boyd Morrison*[1]; [1]William B. Morrison & Associates, 3115 Bayo Vista, Alameda, CA 94501 USA

Decisions on bauxite feed sources affect and direct the very foundation of the alumina refinery siteing process. The chemical and mineralogical composition of the bauxite feed determine process configuration and facility design as well as overall project economics. This drive for an assured source of "quality" bauxite is an ongoing one that never ceases. Existing refineries are continually confronted with bauxite supply issues. These issues dictate the needs to a refinery for: Utilization of the geologically best possible sources located at the best geographic position. Delivery at a reasonable cost. Consistency in processability. Stability in supply. Minimization of environmental risk. More and more the emphasis today for existing alumina refineries is on the word "assured." As the industry's alumina refineries age, so do their bauxite sources. What was once good, cheap, and abundant may not be so now. It should be noted that no new "world class" sources on bauxite have been developed recently. This paper revisits a previous study performed five years ago by again focusing upon the bauxite supply situation as it exists in the industry today. The review covers both existing bauxite sources as well as potential new ones. In doing so it addresses bauxite requirements from the refinery perspective and bauxite production from the source perspective. Differing from the previous paper additional emphasis is placed upon the needs and requirements associated with the initial efforts to identify and confirm potential sources of bauxite through more comprehensive, reliable and target oriented geological analysis. The following will focus upon the bauxite supply situation. Identify where supply problems will emerge if they have not already arisen. Revisit the potential for developing new sources. Evaluate these sources much more extensively from a geological perspective. Look at the economic and political issues of supply and finally update the former cost comparison between existing and potential bauxite sources.

9:20 AM
Greenfield Dilemma - Innovation Challenges: *Peter-Hans ter Weer*[1]; [1]TWS Services and Advise, Imkerweg 5, Huizen 1272 EB The Netherlands

After a long period without greenfield projects, the Aluminium industry is currently considering several greenfield Bauxite/Alumina opportunities worldwide. Many of these potential projects however have difficulty to meet threshold criteria used by the industry for their economic evaluation. This paper provides an insight in aspects of this issue, and it compares the economics of brownfield with greenfield Bauxite/Alumina projects. It concludes with suggested directions that could be explored to improve greenfield project economics.

9:45 AM
Complex System of Long-Term Forecasting of World Markets of Primary Aluminium and Alumina: *B. Arlyuk*[1]; [1]Alumconsult Ltd., 2, Shkiperski protok, St. Petersburg 199106 Russia

The complex system of the long-term forecast of the markets of primary aluminium and metallurgical alumina, taking into account their mutual connections and influence is developed. The system is based on the analytical description of the market connections determining a sales volume and the prices of aluminium and alumina. It has allowed to limit the amount of empirical factors in comparison to usually used econometric approach and has provided the comprehensible significance of model. For an estimation the consumption of primary aluminium at the West the forecasts of development the economics in the Western countries is used, which is characterized by cyclic change of indexes of industrial production. The degree of capacity utilizations of smelters and refineries or the volume of supply of the market in turn depends on a level of the world prices for aluminium and spot prices for alumina. Thus, the system of the forecast takes into account presence of a plenty feedback as inside subsystems of the forecast of the market of aluminium, and also alumina, and between these markets. The developed complex system allows to forecast a degree of capacity utilization of aluminium smelters and alumina refineries in Western countries, balance of supply/consumption of metallurgical alumina and aluminium, alumina spot and contract prices and prices of primary aluminium at LME. Thus as the initial information the forecast of input of new capacities and change of the Western world industrial production are used. Identification of the developed system on the actual quarter data for the period since 1990 till 2004 is executed and the empirical factors of model providing forecasting of the world markets of aluminium and alumina with comprehensible accuracy are determined. The developed system is used for a long term forecasts of the world markets of primary aluminium and metallurgical alumina up to 2015.

10:10 AM Break

10:20 AM
Fundamental Research on Alumina Production of the Future in China: *Qingjie Zhao*[1]; *Qiaofang Yang*[1]; [1]Zhengzhou Research Institute Aluminium Corporation of China, Ltd, R&D Dept., 82,Jiyuan Rd., Shangjie Dist., Zhengzhou, Henan 450041 China

Analyzed is the present research situation on production technology and fundamental theory in the alumina industry, and discussed is the future research situation on it. It is proposed that the developing trends of alumina production technology depends on the two factors, one is that the great achievements obtained should be popularized to intensify the process and reduce energy consumption and cost, the other is that new process and technology should be developed rapidly. The core of the fundamental theory is to provide theoretical and technological support for simplifying the process flow, improving efficiency, reducing the enery consumption and optimizing the production target.

10:45 AM
The Comprehensive Energy Saving in China Alumina Industry: *Lijuan Qi*[1]; *Songqing Gu*[1]; [1]Zhengzhou Research Institute Aluminum Corporation of China, Ltd., R&D Dept., 82,Jiyuan Rd., Shangjie Dist., Zhengzhou, Henan 450041 China

In this paper, analysed are both the present energy consumption of chinese alumina production and the factors affecting energy consumption. The trends of energy consumption in the Chinese alumina production are also proposed, and the key technologies to be developed

and the main measurements to be taken are also put forward in the future Chinese alumina production.

Alumina and Bauxite: Bayer Process Chemistry: Part I

Sponsored by: Light Metals Division, LMD-Aluminum Committee
Program Organizers: Dag Olsen, Hydro Aluminium AS, Porsgrunn 3907 Norway; Travis Galloway, Century Aluminum, Hawesville, KY 42348 USA; Halvor Kvande, Norsk Hydro ASA, Oslo N-0240 Norway

Monday AM Room: 2005
February 14, 2005 Location: Moscone West Convention Center

Session Chair: Robert Bitsch, Alcan, Bauxite & Alumina, Cedex, Gardanne, 13541 France

11:10 AM
Layered Double Hydroxides in the Bayer Process: Past, Present and Future: *Steven Philip Rosenberg*[1]; Lyndon Armstrong[2]; [1]BHP Billiton, Bauxite & Alumina Tech. Ctr., PO Box 344, Collie, Western Australia 6225 Australia; [2]Alcan, Queensland R&D Ctr., PO Box 883, Kenmore, Queensland 4069 Australia

Alumina refiners have been aware of some of the potential uses of Layered Double Hydroxides (LDH's) in the Bayer process for more than a decade. By virtue of the lamellar structure, ability to adjust the distance between these layers, and the reactivity of the interlayer region, LDH's can be used for the controlled addition or removal of a variety of species, both organic and inorganic. In this paper, we review the history and present use of LDH's in alumina refining, particularly the most commonly used calcium and magnesium aluminate varieties. We also examine some of the ways in which these LDH's can be produced in the refinery, both intentional and unintentional, as well as some of the possible reasons thay have not found more widespread application. Finally, we discuss how LDH technology could be applied to deal with emerging trends and issues in alumina refining, particularly in reducing the environmental impact of alumina refining.

11:35 AM
Improving the Bayer Process by Power Ultrasound Induced Crystallization (Sonocrystallization) of Key Impurities: *Graham Ruecroft*[1]; David Hipkiss[1]; Martin Fennell[1]; Linda McCausland[1]; [1]Accentus plc, C3 Technology, 551 Harwell Business Ctr., Didcot, Oxfordshire OX11 0QJ UK

Whilst it is known that precipitation of sodium oxalate in supersaturated solutions can be triggered by adding recycled seed crystals of the same to act as initiator, in practice it is found that the surfaces of the crystals become poisoned by other organic materials present in the liquor, and become inactive as crystal growth initiators. The C3 proprietary Sonocrystallization technology [power ultrasound applied to assist crystallization] works by significantly increasing the frequency of nucleation events in the waste liquor stream compared to current operation. Each nucleation event gives rise to a site for an impurity crystal to form. Consequently, the rate of impurity crystal formation and subsequent removal is greatly enhanced. Importantly, the issue of other organic contaminants inhibiting impurity crystal growth and formation, and therefore their removal, is eliminated.

12:00 PM
Theoretical Research on the Precipitation of Sodium Aluminate Solutions Enhanced by Ultrasound: Shugui Hua[1]; [1]Central South University, College of Chmst. & Cheml. Engrg., Cangsha, Hu'nan China

The heat of formation and frontier orbital of possible monomeric aluminate species, hydroxyl radical(¡¤OH), hydrogen radical(¡¤H) and the products of some reactions in caustic aluminate solutions under ultrasound were computed with a semi-empirical quantum chemical method AM1. According the thermodynamics theory and frontier orbital argument, the structure changes of the solution under ultrasound were studied. Conclusions were made that ultrasound can enhance the formation of the growth unit of crystallization [Al(OH)4£-(H2O)2] and accelerate the precipitation of caustic aluminate solution.

Aluminum Alloys For Packaging

Sponsored by: Light Metals Division, LMD-Aluminum Committee
Program Organizers: Subodh K. Das, Secat, Inc., Coldstream Research Campus, Lexington, KY 40511 USA; Gyan Jha, ARCO Aluminum Inc, Louisville, KY 40223-4032 USA

Monday AM Room: 2002
February 14, 2005 Location: Moscone West Convention Center

Session Chairs: Subodh K. Das, Secat Inc., Lexington, KY 40511 USA; Gyan Jha, ARCO Aluminum Inc., Louisville, KY 40223-4032 USA

8:30 AM
Aluminium Short Term Price Forecast. Speculations on Forwards, Hedging the Sales: *B. Arlyuk*[1]; [1]Alumconsult Ltd., St. Petersburg 199106 Russia

The system has been developed for quantitative and qualitative forecasting of primary aluminium prices at LME up to 3 months ahead using LME daily parameters, as well as monthly statistic data on industrial production indices in Western countries, IP and Dow Jones indexes at USA. The prices forecasting is the basis of the probability approach for determining optimal moments and volumes of transactions with three-month forwards securing maximum profits. The system has been tested by issuance of daily recommendations to a broker for opening and closing of three-month forward positions at LME during four years since July 2000 till June 2004, the pledge initial volume was $1 M and capitalization 80% realized profit for expansion the investments. As optimal is using the limitation for opening new positions 50-55% of pledge to broker. In the average the system is opening new positions of forwards about 60 times per year. The full fixed profit amounted to 250% annually to the initial investments. The system was used during two years for hedging the sales of aluminium within the quarter forward. It gives the opportunity to increase the price of sales by 50 $/t.

9:00 AM
Investigation of Score Corrosion in Aluminum Can Ends: *Gyan Jha*[1]; W. Yin[2]; [1]Arco Aluminum, 9960 Corp. Campus, Ste. 3000, Louisville, KY 40223 USA; [2]SECAT, 1505 Bull Lea Rd., Lexington, KY 40511 USA

Beverage can ends have utilized vinyl and epoxy coatings to protect the Aluminum from corrosion. The coated Aluminum is post lubricated then fabricated into an end. The coating must withstand the fabrication process without any coating adhesion loss, scuffing and coating fracture. In recent years pitting type corrosion has been observed at the score on Aluminum can ends. Score corrosion can lead to premature failure of the Aluminum can end. This paper will discuss the various factors that can effect score corrosion in Aluminum can ends.

9:30 AM
A Mossbauer Study of 3000 and 5000 Series Packaging Alloys: *Gyan Jha*[1]; S. Jha[2]; W. Yin[3]; Ameer Lahamer[4]; [1]Arco Aluminum, 9960 Corp. Campus, Ste. 3000, Louisville, KY 40223 USA; [2](Retired) University of Cincinnati, Physics, Cincinnati, OH 45208 USA; [3]SECAT, 1505 Bull Lea Rd., Lexington, KY 40511 USA; [4]Berea College, Physics, Berea, KY 40404 USA

Understanding Fe and its surroundings in Aluminum alloys 3104 and 5182 has become more important because of the different types of scrap inputs used to cast these alloys. Fe can have an effect on texture and formability of the final rolled product. It is difficult to characterize the nature of Fe with conventional analysis techniques. The study will present results of the analysis of commercial Aluminum packaging alloys by the Mossbauer technique.

10:00 AM
Simulation of Texture-Dependent Recrystallization in 1050 Aluminum: *Anthony D. Rollett*[1]; Joseph Fridy[2]; Hasso Weiland[2]; Jaakko Suni[2]; Abhijit Brahme[1]; [1]Carnegie Mellon University, MSE, 5000 Forbes Ave., Pittsburgh, PA 15213 USA; [2]Alcoa Technical Center, Alcoa Techl. Ctr., PA 15609 USA

In order to verify that we understand the recrystallization process at the microstructural level, Monte Carlo simulation of recrystallization has been undertaken using statistically reconstructed input microstructures to represent the deformed material. This approach has already revealed many gaps in our knowledge of the deformed state, grain boundary properties and so on. A key part of the simulation procedure has been construction of 3D representations of the as-deformed microstructure. The most relevant features are the crystal-

lographic orientations of the grains ("texture") and the size, topology and shape of the grains. In order to perform realistic simulations one needs to specify the initial state of the material with sufficient detail that all these features are reproduced. Cross-sections or surfaces were characterized through automated electron back scatter diffraction (OIM) in the scanning electron microscope (SEM). This approach has shown the importance of capturing the aspect ratio of the deformed grains and the tendency of nuclei to cluster near the prior grain boundaries in order to correctly reproduce the recrystallization kinetics. Work is ongoing to understand the factors that control the marked growth in the cube texture component during recrystallization. Supported in part by the US Department of Energy Aluminum Industry of the Future program.

10:30 AM
Texture-Dependent Recrystallization in 1050 and 5005 Aluminum: Mohammed Haroon Alvi[1]; Hasso Weiland[2]; Jaakko Suni[2]; Soonwuk Cheong[2]; *Anthony D. Rollett*[1]; [1]Carnegie Mellon University, MSE, 5000 Forbes Ave., Pittsburgh, PA 15213 USA; [2]Alcoa Technical Center, PA 15069 USA

Recrystallization kinetics have been studied in hot rolled 1050 and 5005 with the objective of understanding the local variation in the rate of recrystallization as a function of texture component. The overall objective is to decrease annealing times by exploiting such variations. Automated electron back-scatter diffraction (EBSD, or OIM) has been used to quantify microstructures at various stages of recrystallization. Analysis of the grain orientation spread (GOS) was found to be the most effective method for partitioning EBSD maps into recrystallized and unrecrystallized regions. The greatest density of nuclei is observed in the S texture component and the recrystallization kinetics are consequently fastest in grains that have this orientation. The cube component is weak in the as-deformed state but increases to between 25% and 40%, depending on annealing temperature. In related work, we are using these experimental results to validate a computer model of recrystallization.

11:00 AM
Microstructure Evolution in Twin Roll Cast AA3105 During Thermomechanical Processing: *Naiyu Sun*[1]; Burton R. Patterson[1]; Jaakko Suni[2]; Eider A. Simielli[2]; Hasso Weiland[2]; Larry Allard[3]; [1]University of Alabama, Matls. Sci. & Engrg., 1530 3rd Ave. S., BEC 254, Birmingham, AL 35294 USA; [2]Alcoa Technical Center, 100 Techl. Dr., Alcoa Ctr., PA 15069 USA; [3]Oak Ridge National Laboratory, Metals & Ceram. Div., 1 Bethel Valley Rd., PO Box 2008, Oak Ridge, TN 37831-6064 USA

This presentation gives an overview of microstructural evolution during thermomechanical processing of twin roll cast (TRC) AA3105, including homogenization, cold rolling and annealing. The resultant processes of constituent particle coarsening, dispersoid precipitation and recrystallization, and their interaction during various annealing conditions are discussed. Time-temperature-transformation curves were determined for precipitation and recrystallization to understand the interaction of these processes. It was found that homogenization prior to cold rolling had a profound effect on recrystallization kinetics, grain size and gradient, as did homogenization time, temperature and cooling rate. Recrystallization kinetics also increased with decreased casting rate, and increased annealing temperature and heating rate.

11:30 AM
HRTEM Study on the Eutectoid Phase Transformation of the Intermetallic Particles from Al6(Fe,Mn) to α-Al(Mn,Fe)Si Phase in AA3003 Alloy: *Yanjun Li*[1]; Arne Olsen[1]; [1]University of Oslo, Ctr. of Matls. Sci. & Nanotech., Dept. of Physics, PB 1126, Blindern, Oslo 0318 Norway

The phase transformation from Al6(Fe,Mn) to α-Al(Mn,Fe)Si phase in a DC-cast 3003 alloy has been studied by TEM and HRTEM at the early stage of the transformation. The 3-D morphology of the transformed α-Al(Mn,Fe)Si particle containing many cylindrical Al channels has been observed by dark field TEM image. The orientation relationships between the Al6(Fe,Mn), Al-spots, α-Al(Mn,Fe)Si phase, and the surrounding Al matrix has been studied. It has been found that the transformed α-Al(Mn,Fe)Si phase has similar orientation relationships with the matrix as the α-Al(Mn,Fe)Si dispersoids precipitated during heat treatment. Semi-coherent interfaces between the transformed α-phase and the Al matrix and between the Al-spots and the surrounding α-phase have been observed by HRTEM. It suggests that the α-phase has heterogeneously nucleated from the aluminium matrix on the interface between aluminium and Al6(Fe,Mn) particle and the Al-spots has nucleated from the α-phase during the phase transformation.

Aluminum Reduction Technology: Environmental and Modernization

Sponsored by: Light Metals Division, LMD-Aluminum Committee
Program Organizers: Tor Bjarne Pedersen, Elkem Aluminium ANS, Farsund 4551 Norway; Tom Alcorn, Noranda Aluminum Inc., New Madrid, MO 63869 USA; Halvor Kvande, Norsk Hydro ASA, Oslo N-0240 Norway

Monday AM — Room: 2003
February 14, 2005 — Location: Moscone West Convention Center

Session Chair: Margaret M. Hyland, University of Auckland, Dept. of Cheml. & Matls. Engrg., Auckland New Zealand

8:30 AM Invited
Environmental Regulations and Performance for European Smelters: *Eirik Nordheim*[1]; [1]European Aluminium Association, 12, Ave. de Broqueville, Brussels 1150 Belgium

European aluminium smelters are under pressure from tighter environmental regulations and also increasingly Environmental Quality Standards. Emission limits to air, water and waste deposits are set based on common EU regulations. These will generally be framework regulations, leaving the Member States to set detailed limits. But some regional groups like OSPARCOM have in addition to this recommended specific emissions limits to air and water. Increasingly also the Air Quality Standards and Water Quality Standards currently being set at EU level will have an impact on the emission limits set for individual plants, due to the contribution from smelter emissions on the local environment. The presentation will look at the relevant emission limits and Enviromental Quality Standards and where the smelters are in relation to this.

8:55 AM
PFC Emissions Performance for the Global Primary Aluminum Industry: *Jerry Y. Marks*[1]; [1]International Aluminium Institute, 312 NE Brockton Dr., Lees Summit, MO 64064 USA

The global primary aluminum industry, through its new Global Aluminum Sustainable Development Initiative (GADSI), has set a number of challenging environmental targets. Greenhouse Gas Emissions Reduction is one of the focal points of the initiative. A global industry perfluorocarbon (PFC) specific emissions reduction target of 80% has been set for 2010 relative to 1990. To monitor PFC emissions reductions an annual survey of anode effect performance is carried out by the International Aluminium Institute (IAI). IAI is working with a number of world organizations to assure the homogenous application of accurate and transparent GHG inventory methodology. This paper will discuss the results of the anode effect performance surveys through 2003, the latest year for which survey information is available, and will examine benchmark performance by reduction technology. The paper also discusses progress in efforts aimed at establishing common GHG calculation and inventory methods.

9:20 AM
Environmental Challenges in the Prebake Line at Hydro Aluminium Karmøy: *Jørn Tonheim*[1]; Knut Arne Paulsen[1]; Roald Holten[1]; Arnt Helge Fidjeland[1]; Harald Martinsen[1]; Kirsten Louise Bolstad Halvorsen[1]; [1]Hydro Aluminium Karmøy, N-4265 Håvik Norway

It is a challenge for aluminium smelters to reduce emissions and to keep a good working environment. There are still cases of occupational asthma, even in the most modern aluminium smelters. In the Prebake line at Hydro Aluminium Karmøy the emissions of fluoride and dust are within the threshold limits set by the Government according to the OSPAR convention. However, the limits regarding dust and fluoride in the working environment have often been exceeded during anode change. To reduce these emissions and improve the working environment, different measures have been carried out. Forced suction was implemented on 14 test pots in spring 2003 and will be implemented in the whole Prebake line by January 2005. Automatic positioning of the anodes after anode change was implemented during the spring in 2004. A test with reduced manual control in conjunction with use of cavity cleaner before setting the new anode has also been performed.

9:45 AM
Understanding Fugitive Fluoride Emissions at Alumar Consortium: *Nilton Freixo Nagem*[1]; Eliezer S. Batista[1]; Ari F. Silva[1]; Valerio A. Gomes[1]; Luciano J.P. Souza[1]; Luis Carlos A. Venancio[1]; [1]Consórcio

de Aluminio do Maranhão - Alumar, Smelter, Br 135, Km 18 - Distrito Industrial de Pedrinhas, São Luis, Maranhão 65095604 Brazil

One of the most control demanding activities in a Smelter is fugitive fluoride emissions (HF) monitoring and control in Potrooms. A study was performed in Alumar Smelter to map and determine the impact of unit operations (anode setting and tapping, among others) in Potrooms fugitive fluoride emissions (HF). This study consisted on a continuous monitoring of gaseous fluoride through the use of an Open-Path Tunable Diode Laser (TDL) equipment and its correlation with some process variables such as bath chemistry, current level and alumina LOI.

10:10 AM Break

10:25 AM
Why the Søderberg Technology Has a Future in Mini-Smelters Intergrating a Coal Fired Power Plant: *Andre Teissier-duCros*[1]; [1]GEANOVERSEAS, Gean-KTD Mini Smelter Proj., 4434 Covington Hwy., Atlanta, GA 30035-1212 USA

A State of the Art Soderberg incorporating all known, proven technologies, equipment and know how regarding emission control will meet future environment, health and safety standards (OSPAR guidelines) and be bankable for a greenfield, especially if combined with a fluidized bed boiler power plant enjoying itself a low CO2 level on top of other low emission performance. Issues to address are CO2, CF4, HF and mostly PAH (operators' safety & health). We will review the "package" of operating procedures, quality of anode paste, process control settings co-ordinating anode movements and point feeding frequency, and specifications of all equipment. This opens a new market for greenfields in countries suffering of high energy cost and fast growing energy demand.

10:50 AM
CD20 Reduction Cell Upgrade for Dubal's Expansion Project: *Yousef Ali AlFarsi*[1]; Abdelhamid Meghlaoui[1]; Najeeba AlJabri[1]; [1]Dubai Aluminium Company Ltd., Tech. Dvlp., PO Box 3627, Dubai United Arab Emirates

Dubai Aluminium Company Limited (DUBAL) has 480 CD20 reduction cells designed for operation at 200 kA. In planning for a plant expansion, the Technology Development function was entrusted the challenge to effect design criteria changes to the CD20 cell, without prototyping, targeting an operating amperage of 220-230 kA in order to increase the production from 560,000 mt/year to 760,000 mt/year. Such changes to the CD20 technology were critical for the capital cost and the operating cost reduction. The learning curve associated with six years of improvements in operational practices, process control and thermal-electrical design validation of the CD20 and CD26 technologies resulted in appropriate improvements of CD20 cell design and control. Modifications to cathode lining and geometry were supported by mathematical modeling and experimental correlation. Dubal code-named the new reduction cell "D20". In 2003, DUBAL installed and commissioned 212 D20 cells that are operating very satisfactorily at 220 kA, including 50 cells with graphitised cathodes operating at 225 kA in a dedicated booster section. This paper covers the development of the D20 cell, as well as one-year key operating parameters.

11:15 AM
Energy Saving in Hindalco's Aluminium Smelter: *S. C. Tandon*[1]; R. N. Prasad[1]; [1]Hindalco Industries Ltd., Renukoot-231 217, Sonebhadra, UP India

The electrolytic production of primary aluminium metal in Hall-Heroult cells is highly energy intensive and accounts for nearly 40% of the production cost. The role of electric current in aluminium electrolysis cell is two fold; one is the electrolysis of alumina to produce aluminium metal as per Faraday's law of electrolysis and other is maintaining thermal balance of electrolytic cells to make them workable which accounts for more specific energy consumption than theoretically required. Hindalco has made serious efforts to modernize its vintage cells of 1950's & other facilities in order to reduce energy consumption and improve the working environment. Various technological developments have been introduced over the years leading to significant changes in cathode design, alumina feeding, cell process control, operating strategies and ancillary equipment resulting in substantially improved technical results. Recent introduction of slotted anode along with few other initiatives have further reduced power consumption by 0,3 kWh/MT Al, leading to an energy consumption below 14,0 DC kWh/MT Al in vintage cells of the 1950's.

11:40 AM
Alro's Creep Capacity Expansion: *Gheorghe Dobra*[1]; Satish Manaktala[1]; Mihail Atanasiu[1]; Constantin Radulescu[1]; Cristian Theodor Stanescu[1]; [1]ALRO, Techl., 116, Pitesti St., Slatina 230104 Romania

Alro, the only aluminium smelter in Romania, was built under the Romanian socialist system in the 1970s. Transition to a market based economic system, clearly showed that the smelter based on Pechiney AP 9 pre-bake technology had to modernise in order to remain competitive and to meet the EU environmental standards. In the 1990s, a major modernisation program at the cost of over $120 million was undertaken to refurbish the plant. At the completion of this program, the Smelter provided an ideal platform for increasing the electrolytic cell capability significantly and much beyond its original design. A test section with booster power, redesigned cathodes and larger anodes was established and the cell performance results confirmed the potential to increase the Smelter capacity by nearly 30 percent and reduce the energy consumption by over 5%. These results have led to establishment of a Smelter creep capacity expansion program due to be completed by the end of 2005. The test section operation methodology and performance results are the subject of this paper.

Arsenic Metallurgy: Fundamentals & Applications: Plenary Session

Sponsored by: Extraction & Processing Division, EPD-Copper, Nickel, Cobalt Committee, EPD-Process Fundamentals Committee, EPD-Pyrometallurgy Committee, LMD/EPD-Recycling Committee
Program Organizers: Ramana G. Reddy, University of Alabama, Department of Metals and Materials Engineering, Tuscaloosa, AL 35487-0202 USA; V. Ram Ramachandran, Scottsdale, AZ 85262-1352 USA

Monday AM Room: 2014
February 14, 2005 Location: Moscone West Convention Center

Session Chairs: V. Ram Ramachandran, Scottsdale, AZ 85262-1352 USA; Ramana G. Reddy, University of Alabama, Dept. of Metals & Matls. Engrg., Tuscaloosa, AL 35401-0202 USA

8:30 AM
The Removal of Arsenic from Aqueous Solution by Coprecipitation with Fe(III): *Larry G. Twidwell*[1]; Robert G. Robins[2]; Jacob W. Hohn[1]; [1]Montana Tech of University of Montana, Sch. of Mines & Engrg., 1300 W. Park St., Butte, MT 59701 USA; [2]Murdock University, Chmst., Western Australia 6150 Australia

In treating hydrometallurgical solutions and waste streams for the removal of arsenic, the use of coprecipitation with Fe(III) has been specified by the U.S. EPA as the Best Demonstrated Available Technology. This technology has been widely adopted over the last century, and developments have been well reviewed. This paper is aimed at clarifying a number of uncertainties and misconceptions that result from previously published work by many authors. The clarification will include a discussion of the importance of Fe:As mole ratio, initial arsenic concentration, arsenic valence state, the effect of mixed arsenic valence states, system agitation rate, and possible modifications to the ferrihydrite structure on the effectiveness of arsenic removal. A comparison of the effectiveness of arsenic removal by ferrihydrite coprecipitation, post precipitation, and granulated ferrihydrite will be presented. Also, ferrihydrite long term stability will be discussed.

9:00 AM
On the Preparation and Stability of Scorodite: *George P. Demopoulos*[1]; [1]McGill University, Metals & Matls. Engrg., 3610 Univ. St., Montreal, Quebec H3A 2B2 Canada

Scorodite is advocated as a viable option for the fixation of arsenic from aqueous process effluents, especially for arsenic-rich and iron-deficient solutions. It has a high arsenic content, it requires stoichiometric amounts of iron, and it has excellent dewatering and disposal characteristics. Because of its high degree of crystallinity and small specific surface area, scorodite is also, very importantly, thought to have high inherent stability at least from a kinetic point of view. As a mineral, scorodite can be found in a wide variety of geological settings. This suggests that it is stable under specific weathering conditions. Hence our interest in designing a cost-effective process for returning arsenic to the environment in this mineral form. In this paper, (1) the preparation of scorodite in lime neutralisation ?type circuits is discussed and (2) the long term stability of scorodite is evaluated in the light of newly generated accelerated ageing kinetic data.

9:30 AM Break

9:45 AM
Arsenic Capacity of Copper Slags: *R. G. Reddy*[1]; J. C. Font[1]; [1]University of Alabama, Metallurgl. & Matls. Engrg., PO Box 870202, Tuscaloosa, AL 35487-0202 USA

Arsenic capacity modeling and experimental study between mattes and slags in copper smelting is reviewed. The arsenic capacities of slags are calculated a priori using Reddy-Blander model. The effect of matte and slag compositions, PSO2 and temperatures on arsenic capacities of copper slags is made. The calculated results for arsenic capacities are in good agreement with the available experimental data. Application of this model for the prediction of Arsenic capacities and distribution ratios in mattes and slags, and removal of arsenic in several industrial smelter processes is discussed.

10:15 AM
Arsenic and Old Waste: *Donald A. Robbins*[1]; [1]ASARCO, Inc., Environmental Services, Phoenix, AZ 85016 USA

Asarco has had a long involvement with arsenic. As far back as the turn of the last century, Asarco was a producer of arsenic trioxide. Later, through the efforts of its Central Research Laboratory, value added products such as high purity metallic arsenic and gallium arsenide were produced. During these years of arsenic production, Asarco was a pioneer in industrial hygiene programs for its workers exposed to arsenic. Biological monitoring programs were initiated and criteria developed to guide industrial hygiene and safety personnel in application of respiratory protection, ventilation, personal protective gear, and education for protecting its workers. With the advent of CERCLA and RCRA in 1980 ASARCO's issues related to arsenic became very different. The company became involved in a significant number of remediation sites where work is on going to prevent arsenic and other metals from being released into the environment. These remediation sites are fertile venues for the application of cost effective and creative control technologies particularly for arsenic.

Beta Titanium Alloys of the 00's: Applications I

Sponsored by: Structural Materials Division, SMD-Titanium Committee
Program Organizers: Rod R. Boyer, Boeing Company, Metall./6-20J1, Seattle, WA 98124-2207 USA; Robert F. Denkenberger, Ladish Co., Inc., Cudahy, WI 53110-8902 USA; John C. Fanning, TIMET, Henderson, NV 89009 USA; Henry J. Rack, Clemson University, School of Materials Science & Engineering, Clemson, SC 29634-0921 USA

Monday AM Room: Salon 10/11
February 14, 2005 Location: San Francisco Marriott

Session Chairs: Henry J. Rack, Clemson University, Matls. Sci. & Engrg., Clemson, SC 29634-0921 USA; Robert D. Briggs, Boeing Company, Boeing Commercial Airplane, Seattle, WA 98027 USA

8:30 AM Opening Comments

8:40 AM
The Use of Beta Titanium Alloys in the Aerospace Industry: *Rodney Raymond Boyer*[1]; Robert David Briggs[1]; [1]The Boeing Co., Metall./6-20J1, PO Box 3707, MS 73-44, Seattle, WA 98124 USA

Beta titanium alloys have been available since the 1950's (Ti-13V-11Cr-3Mo or B12VCA) but significant applications of these alloys - beyond the SR-71 Blackbird - had been slow in coming. The next significant usage of a beta-alloy did not occur until the mid 1980's on the B-1 bomber. This aircraft utilized Ti-15V-3Cr-3Al-3Sn sheet because of the capability for strip rolling, improved formability and higher strength. The next major usage was on a commercial aircraft, the Boeing 777 which made extensive use of Ti-10V-2Fe-3Al high-strength forgings. Ti-15V-3Cr-3Al-3Sn ducting, castings and springs were also used, along with Ti-3Al-8V-6Cr-4Mo-4Zr (Beta-C) springs. More recent work at Boeing has focused on the development of Ti-5Al-5Mo-5V-3Mo, a high strength alloy which can be used at higher strength than Ti-10V-2Fe-3Al and is much more robust - it has a much wider or friendlier processing window. This, along with additional studies at Boeing, and from within the aerospace industry in general will be discussed in detail, summarizing applications and the rationale for the selection of this alloy system for aerospace applications.

9:10 AM
Military Applications for Beta Alloys: *John C. Fanning*[1]; [1]TIMET, Henderson, NV 89009 USA

Beta alloys are potentially useful for numerous non-aerospace military applications. Topics to be discussed in this paper include: evaluation of TIMETAL 15-3 for body armor; fabrication and evaluation of a TIMETAL 21S mortar barrel; use of TIMETAL 15-3 for tactical knives; and resistance of TIMETAL 21S to erosion in a cannon barrel.

9:40 AM
Application of Ti-10-2-3 in Rotor Hub Parts of EUROCOPTER: *G. Antoine*[1]; Jerome Panter[2]; [1]EUROCOPTER; [2]EADS, Corp. Rsch. Ctr., 12 rue Pasteur, Suresnes 92150 France

The need for maximum lightening in highly fatigue stressed parts of helicopters, e.g. hub bodies, blades sleeves, ..., has led for a number of structural parts of the last EUROCOPTER programs to the use of the Beta titanium alloy Ti 10.2.3 in place of steels. This choice which is motivated by the research of the best weight/cost/strength compromise was favourable to Ti10.2.3 due to its great fatigue behaviour and to the fact that it enable to remove the environmental unfriendly cadmium plating needed on conventional steels. This introduction was possible due to joint researches between EUROCOPTER and EADS Corporate Research Center, especially for metallurgical and mechanical characterizations. This paper will present a summary of the work done in the joint research program and will present the different applications of Ti10.2.3 on the last EUROCOPTER programs as EC120 and NH90.

10:05 AM
Implementation of Dynamic Grade Ti-10V-2Fe-3Al Forgings on the RAH-66 Comanche Helicopter: *Michael J. Lutian*[1]; [1]Sikorsky Aircraft Corp., 6900 Main St., PO Box 9729, Stratford, CT 06615-9129 USA

A number of new materials technologies (metallic and non-metallic) were developed and qualified for the Comanche Program. This paper will focus on one of the primary materials technology developments, triple-melt dynamic grade Ti-10V-2Fe-3Al forgings. A summary of the die forging applications being qualified on critical Comanche main rotor system and airframe interface components, ranging from 10 to 900 pounds, is described. First article qualification and lot acceptance forging data from over twenty destructively-tested forgings representing a dozen part numbers and several forging suppliers, forged over a ten year period during the DVP and EMD Phases of the Comanche Program, will be presented. Data will include analysis of several hundred tensile, fatigue, and fracture toughness coupon tests. Results support triple-melt dynamic grade Ti-10V-2Fe-3Al as a forging material possessing a superior, balanced combination of mechanical properties, producible in a wide range of forging sizes, for optimized designs of critical dynamic components.

10:30 AM Break

10:45 AM
Beta Titanium Springs in the 00's: *Charles Pepka*[1]; [1]Renton Coil Spring, PO Box 880, 425 S. 7th St., Renton, Washington 98055 USA

World class engineers in the new millennium will bring the demands, of cost, reliability, lighter weight, consistent supply, longer service life, and lower cost! These points are all interconnected and cannot be considered separately. Lowering product cost alone will not insure a future in the world marketplace. This market is requiring quality, reliability, at a cost. Beta Titanium like 3-8-6-4-4 (Beta C) springs will provide an innovative engineering team with the tools to meet their needs. AMS spec 4957 Wire and 4958 bar specifications are the most widely used Titanium materials certified for springs. Together they give a stable foundation for titanium's usage into the new millennium. Applications for titanium springs are varied. They range form Space, Commercial Aircraft, Military Aircraft, Military Equipment, many forms of racing (Automotive, Motorcycles, quads, etc.) chemical and industrial applications. The reasons for their usage center around a performance envelope consisting of the smallest lightest package for the force required to do the job. Users report an increase in their equipments performance after switching from other materials to Titanium. The presentation will include a design study and actual applications of Titanium springs.

11:15 AM
Production of Beta Alloys by Electron-Beam Single-Melting: *Michelle McCann*[1]; David Tripp[2]; Michael Cardamone[3]; John C. Fanning[1]; Jon Quinn[3]; [1]TIMET, PO Box 2128, Henderson, NV 89009 USA; [2]TIMET, 900 Hemlock Rd., Morgantown, PA 19543 USA; [3]TIMET, 100 Titanium Way, Toronto, OH 43964 USA

Beta alloys provide useful combinations of mechanical and physical properties, but widespread usage is often limited by the relatively high cost. Production by Electron-Beam Single-Melting (EBSM) may provide opportunities for significant cost reduction related to ingot shape, increased scrap utilization and economies of scale. This technology has already enabled the implementation of Ti-6Al-4V in ground combat vehicle systems and other cost-sensitive applications. Since the EBSM production method is substantially different from the traditional vacuum arc re-melting (VAR) production method, extensive testing and evaluation will be performed on the EBSM product to ensure that the properties and quality are equivalent to those of the traditional product. Results of recent studies on the potential production of beta alloys by EBSM will be discussed in this paper.

11:40 AM
Single Melt Beta-C for Spring and Fastener Applications: *K. O. Yu*[1]; E. M. Crist[1]; R. Pesa[2]; N. Cecchini[2]; C. M. Bugle[2]; [1]RMI Titanium Company, PO Box 269, 1000 Warren Ave., Niles, OH 44446-0269 USA; [2]Dynamet Incorporated, Washington, PA USA

Beta-C is a high strength titanium alloy widely used for spring and fastener applications. Spring and fastener input stock is currently manufactured by rolling billets forged from conventional double melt VAR (2 x VAR) ingots. Recent advances in plasma arc melting (PAM) single melt technology offer a potential to reduce the input stock cost by directly rolling the as-cast near net shape PAM ingots instead of the conventional forged billets. A 5" diameter as-cast PAM ingot was rolled to 0.60" bars which were then processed to smaller diameter centerless ground bars for making springs and fasteners. The evaluation of microstructures and mechanical properties of the bar input stock as well as the finished spring and fastener stock will be presented.

Biological Materials Science and Engineering: Biological Materials I

Sponsored by: Structural Materials Division, Electronic, Magnetic & Photonic Materials Division, Society for Biomaterials, Surfaces in Biomaterials Foundation, SMD-Mechanical Behavior of Materials-(Jt. ASM-MSCTS), EMPMD/SMD-Biomaterials Committee
Program Organizers: Marc Andre Meyers, University of California, Department of Mechanical and Aerospace Engineering, La Jolla, CA 92093-0411 USA; Sungho Jin, University of California, Department of Materials Science, La Jolla, CA 92093 USA; Roger J. Narayan, Georgia Tech, School of Materials Science and Engineering, Atlanta, GA 30332-0245 USA

Monday AM Room: 3009
February 14, 2005 Location: Moscone West Convention Center

Session Chairs: Marc Andre Meyers, University of California, Matls. Sci. & Engrg., La Jolla, CA 92093-0411 USA; Julian Vincent, University of Bath, Dept. of Mechl. Engrg., Bath BA2 7AY UK

8:30 AM Keynote
Mechanical Properties of Biological Materials: *Julian Vincent*[1]; [1]University of Bath, Dept. of Mechl. Engrg., Bath BA2 7AY UK

It seems to me that the mechanical properties of biological materials are of interest to the engineer for 3 main reasons: What characteristics do they have? Why and how? How can we benefit from this information? The most versatile material is probably the cuticle of arthropods, which has to be skeleton, skin and sensor, providing support, flexibility, sensitivity, protection, waterproofing, absorption, locomotion, etc. In providing this it is impossible to separate structure and material properties. The properties (examples in parentheses) therefore have to be understood at the level of chemical bonding (epitaxy of chitin-protein interactions via silk-like conformations; incorporation of heavy metals), physical chemistry (control of stiffness achieved by control of water content), micro-morphology (fibre orientations; volume fractions), macromorphology (control of buckling by folding stiffeners) and function (wing foldings, mechanisms for drilling holes). The benefit comes from comparing the design philosophy of the arthropod with what we would do given our technical background and experience. These turn out to be very different (there's only a 10% overlap - by design or coincidence) suggesting that 90% of biological problem-solving remains to be explored and exploited. The last part of the talk will therefore be devoted to techniques of biomimetic data-mining and how to organise biological information in a way which will aid creativity and innovation.

9:15 AM Invited
A Materials Science Approach to the Fracture and Fatigue Resistance of Hard Mineralized Tissue: *R. O. Ritchie*[1]; R. K. Nalla[1]; J. J. Kruzic[1]; J. H. Kinney[2]; [1]University of California, Matls. Sci. & Engrg., 381 Hearst Mining Bldg., MC 1760, Berkeley, CA 94720-1760 USA; [2]Lawrence Livermore National Laboratory, 700 East Ave., Livermore, CA 94550 USA

Despite the clinical interest in the fracture resistance of hard mineralized tissues such as bone and dentin, there is only limited mechanistic information available on how these materials derive their toughness, how it is affected by microstructure and orientation, and how behavior is specifically affected by cyclic fatigue loading. In the present study, crack-growth behavior in dentin and bone is characterized using a fracture-mechanics approach. Significant extrinsic toughening, specifically from crack bridging, crack deflection and (to a lesser extent) microcracking is found; such crack-tip shielding mechanisms naturally induce resistance-curve behavior in an analogous way to the toughening of structural. In this presentation, we discuss the origin of such toughening, e.g., crack bridging from collagen fibrils and uncracked ligaments, and describe how such mechanisms are controlled by the hierarchical microstructure of these biological materials. Moreover, we address the issue of subcritical (time- and cycle-dependent) cracking and why these materials degrade with age.

9:45 AM
Osteoblast-Like Cell Mineralization Induced by Multiphasic Calcium Phosphate Ceramic: *Reed Ayers*[1]; Sheila Nielsen-Preiss[2]; Virginia Ferguson[1]; John J. Moore[1]; Hans-Joachim Kleebe[1]; [1]Colorado School of Mines, CCACS, 1500 Illinois St., Golden, CO 80401 USA; [2]University of Colorado Health Sciences Center, S/M Endocrinology/Metabolism/Diabetes Di, 4200 E. Ninth Ave., CB A009/111H, Denver, CO 80262 USA

The work presented here examines the effect of multiphasic CaP materials on the activity of Saos-2 osteoblast like cells. Heterogeneous calcium phosphate (HCaP) was synthesized using self-propagating high temperature combustion synthesis (SHS). All samples were characterized using XRD, SEM, and FTIR. Cell culture procedures of CaP with Saos-2 cells followed ASTM 813-01. Samples were examined by Environmental SEM (ESEM) and EDS to characterize the mineral content of the cultures. Gold coated samples were used for high resolution imaging. Biomineralization was noted in unconditioned cultures exposed HCaP while the controls (cells only in media and HCaP only in media) showed no mineralization. Calcium phosphate plate-like structures were seen adjacent to cells expressing calcium phosphate containing vesicles. These structures are similar to the organophosphate crystals seen in previous work. Plate-like crystals were also noted in the larger membrane vesicles on the Saos-2 cells indicating the biomineralization was being cellularly mediated.

10:05 AM Break

10:20 AM
Phase Dependent Fracture of Polytetrafluoroethylene (PTFE): *Eric Nathaniel Brown*[1]; G. Rusty Gray[2]; Dana M. Dattelbaum[3]; [1]Los Alamos National Laboratory, Matls. Sci. & Tech., TA-35, Bldg. 455, DCDP 01S, MS E544, Los Alamos, NM 87545 USA; [2]Los Alamos National Laboratory, Matls. Sci. & Tech., MS G755, Los Alamos, NM 87545 USA; [3]Los Alamos National Laboratory, Dynamic Experimentation, MS P952, Los Alamos, NM 87545 USA

Compared with other polymers, polytetrafluoroethylene (PTFE) presents an extremely low coefficient of friction and excellent chemical and thermal stability. This has lead to a wide range of applications for biological implants ranging from single component PTFE structures to sliding contact pads in complex joints, as well as numerous other failure sensitive applications. However, the failure mechanisms of PTFE have received relatively little investigation. Polytetrafluoroethylene is semi-crystalline in nature with its linear chains forming complicated phases near room temperature and ambient pressure. Due to the presence of three unique phases near room temperature, failure during standard operating conditions is strongly phase dependent. This paper presents a comprehensive and systematic study of fracture and damage evolution in pedigreed PTFE 7C to elicit the effects of temperature-induced phase on fracture mechanisms. Fracture behavior is observed to undergo transitions from brittle-fracture below 19°C to ductile-fracture with fibril formation and large-scale plasticity over 30°C.

10:40 AM Cancelled
Electromagnetic-Thermal Responses of Tissues During Microwave Hyperthermia

11:00 AM
Mechanistic Aspects of the Fatigue Behavior of Mineralized Tissues: *Jamie J. Kruzic*[1]; Ravi K. Nalla[2]; John H. Kinney[3]; Robert O. Ritchie[2]; [1]Oregon State University, Dept. of Mechl. Engrg., 204 Rogers Hall, Corvallis, OR 97331 USA; [2]Lawrence Berkeley National Laboratory, Matls. Scis. Div., 1 Cyclotron Rd., Bldg. 62R0100-8255, Berkeley, CA 94720-8139 USA; [3]Lawrence Livermore National Laboratory, 700 East Ave., Livermore, CA 94550 USA

The failure of cortical bone and dentin due to repetitive cyclic loading is a problem of considerable clinical significance. Accordingly, in vitro fatigue-crack growth experiments were performed on human cortical bone (34-41 year-old humeri) and elephant dentin specimens in Hanks' Balanced Salt Solution with the goal of understanding the mechanisms of fatigue-crack propagation. Fatigue-crack growth rates, da/dN, were measured and characterized in terms of the stress intensity range, ΔK. Additionally, subcritical crack-growth experiments were conducted under sustained (static) loading to determine if fatigue-crack growth is due to repetitive loading and unloading, or simply a function of the maximum stress intensity. In both cases, a regime was found where a true cyclic-fatigue mechanism exists; however, for human cortical bone at growth rates above ~ 5 x 10^{-7} m/cycle, both cyclic loading and sustained loading at the maximum stress intensity yielded similar behavior. For the regime of behavior where cyclic loading is required to achieve crack propagation, a fatigue mechanism of alternating crack blunting and resharpening is proposed for both tissues.

11:20 AM
Mechanical Behavior and Structure of a Toco Toucan Beak: *Yasuaki Seki*[1]; Matthew S. Schneider[1]; Marc A. Meyers[1]; Bimal Kad[2]; Franck Grignon[1]; [1]University of California, Dept. of MAE 0411, 9500 Gilman Dr., La Jolla, CA 92093-0411 USA; [2]University of California, Dept. of Structl. Engrg., 9500 Gilman Dr., La Jolla, CA 92093-0085 USA

Composite sandwich structures of biomaterials are found throughout nature. Toucan beaks are an excellent example of this. The beaks are 1/3 the length of the bird, yet only make up about 1/20 of the birds mass. In this study, the structure and mechanical properties of a Toco Toucan beak was studied. It was found to be a sandwich composite with an exterior of keratin and a fibrous network of open cells made of calcium rich proteins. The keratin layer was comprised of many small hexagonal bricks glued together. The mechanical properties of the keratin layer revealed a tensile strength of about 50 MPa and a Young's modulus of 2 GPa. Additional measurements taken using micro- and nanoindentation hardness corroborated these values. The keratin layer also had a viscoplastic behavior with changing modes of deformation from slippage due to release of the organic glue at low strain rates to fracture of the keratin bricks at higher strain rates. The fracture surfaces were images with SEM and models of failure behavior are presented.

11:40 AM
Viscoelastic Behavior of Human Stratum Corneum: *Kenneth S. Wu*[1]; Eilidh Bedford[2]; David J. Moore[3]; Reinhold H. Dauskardt[1]; [1]Stanford University, Matls. Sci. & Engrg., 416 Escondido Mall, Bldg. 550, Stanford, CA 94305-2205 USA; [2]Unilever Research and Development, Port Sunlight CH63 3JW UK; [3]Unilever Research and Development, Edgewater, NJ 07020 USA

The outermost layer of skin, or stratum corneum (SC), provides mechanical and permeability barrier protection from the external environment. The mechanical behavior of SC is crucial to its function and related to underlying cellular microstructure. The influences of temperature, hydration, and tissue treatments have received some attention, but investigations frequently ignore underlying viscoelastic and molecular relaxation processes. These processes are systematically explored here using dynamic and transient mechanical tests involving creep-recovery and stress-relaxation experiments. The influences of hydration, temperature, and chemical modification of the SC tissue were explored. Chemical treatment included delipidization and exposure to buffered pH solutions that modify intercellular lipid properties. Time scales associated with SC viscoelasticity are reported and related to underlying molecular relaxation processes. Stretched exponential modeling of the behavior provides a measure of the distribution of relaxation time scales and their dependence on conditioning parameters. Relaxation processes in the SC are shown to be dominated by long time scales with softening effects from increasing SC hydration significantly decreasing relaxation times.

12:00 PM
Mechanisms Governing the Inelastic Deformation of Cortical Bone: *Christopher Mercer*[1]; Rizhi Wang[2]; Anthony G. Evans[1]; [1]University of California, Matls. Dept., Engrg. II, Rm. 1355, Santa Barbara, CA 93106 USA; [2]University of British Columbia, Dept. of Metals & Matls. Engrg., Forward Bldg., Rm. 107, 6350 Stores Rd., Vancouver, BC V6T 1Z4 Canada

A two-part investigation has been conducted to understand the inelastic response of cortical bone. In the first part, a flexural test protocol has been designed and implemented that monitors the axial and transverse strains on both the tensile and compressive surfaces of cortical bovine bone. The results are used to assess the relative contributions of dilatation and shear to the inelastic deformation. A deconvolution procedure has been employed to affirm that the stress/strain curves in tension and compression are consistent with results in the literature. Unload/reload tests have characterized the hysteresis and provided insight about the mechanisms causing the strain. In the second part of the investigation, a model is devised for the intrinsic stress/strain response of bone, based on a recent assessment of the nano-scale organization of the collagen fibrils and mineral platelets. The model is used to rationalize the inelastic deformation in tension, as well as the permanent strain and hysteresis.

Bulk Metallic Glasses: Processing and Fabrication I

Sponsored by: Structural Materials Division, SMD-Mechanical Behavior of Materials-(Jt. ASM-MSCTS)
Program Organizers: Peter K. Liaw, University of Tennessee, Materials Science and Engineering, Knoxville, TN 37996-2200 USA; Raymond A. Buchanan, University of Tennessee, Materials Science and Engineering, Knoxville, TN 37996-2200 USA

Monday AM — Room: 3006
February 14, 2005 — Location: Moscone West Convention Center

Session Chairs: Peter K. Liaw, University of Tennessee, Matls. Sci. & Engrg., Knoxville, TN 37996 USA; Raymond A. Buchanan, University of Tennessee, Matls. Sci. & Engrg., Knoxville, TN 37996 USA

8:30 AM Opening Remarks

8:35 AM
Prediction of the Constitution of Metallic Glasses: *Daniel Miracle*[1]; [1]Air Force Research Laboratory, Matls. & Mfg. Direct., 2230 Tenth St., Wright-Patterson AFB, OH 45433 USA

Previous structural models show broad consistency with selected metallic glass features, but do not provided a convincing predictive capability for important characteristics, including constitution. An earlier model for the stability of metallic glasses by Egami and Waseda enabled a reasonable ability to predict the concentration of binary metallic glasses, but there has been no progress since in predicting or explaining the rich and confusing breadth of metallic glass constitutions for more complex glasses. An atomic structural model for metallic glasses has very recently been established. Using relative atomic sizes as the primary variable, this model provides a convincing ability to predict the constitution of metallic glasses with as many as seven chemically distinct constituents in glasses based on Zr, Pd, Fe, Mg, Ti, Al and rare earth metals. The features of this model will be briefly outlined, and comparison with between predicted and observed glass compositions will be presented and discussed. Predictions for medium-range atomic order and local coordination numbers will also be compared with experiment.

8:55 AM
Ti-Base Bulk Nanostructured Composite: *Jürgen Eckert*[1]; *Jayanta Das*[1]; Guo He[2]; Wolfgang Löser[3]; [1]Technische Universität Darmstadt, FB11 Matl. und Geowissenschaften, FG Physikalische Metallkunde, Petersenstrasse 23, Darmstadt, D-64287 Germany; [2]National Institute for Materials Science, Light Matl. Grp., 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047 Japan; [3]Leibniz-Institut für Festkörper- und Werkstoffforschung Dresden, Postfach 270016, D-01171 Dresden Germany

The in situ formation of bulk metallic glass based composites has recently been demonstrated in several multi-component alloy systems, where a strong glassy matrix is combined with a ductile dendritic ß-Ti type solid solution as the toughening phase. Taking advantage of the hints provided by this successful approach, we developed a strategy for the design of primary-dendrite/nano-eutectic in situ Ti-base bulk composites that can lead to simultaneous high strength and ductility. Our approach employs copper mold casting for the production of bulk alloys, and the solidified microstructure is designed to be composed of micrometer-sized ductile dendrites uniformly distributed inside a ma-

trix of nanoscale eutectic reaction products. The nanostructured matrix is achieved at a relatively deep eutectic, which facilitates the formation of a nano/ultrafine eutectic microstructure over a range of cooling rates. The multicomponent recipe stabilizes a ductile solid solution as the toughening phase and helps reduce the eutectic spacing down to nanometer scale. The observed microstructures will be described under consideration of the solidification parameters and the conditions required to form a nanostructured composite, and we will also correlate the microstructure with the mechanical properties to demonstrate the desirable high strength and plasticity.

9:15 AM
Development of Fe-Based Bulk Amorphous Alloys: From Theory to Experiment: *Z. P. Lu*[1]; C. T. Liu[1]; [1]Oak Ridge National Laboratory, Metals & Ceram. Div., Oak Ridge, TN 37831-6115 USA

Glass formation is always a competing process between liquid phase and resulting crystalline phases. Either enhancing the liquid phase stability or suppressing the formation of competing crystalline phase would greatly enhance the glass-forming ability (GFA) of glass-forming liquids. Based on these concepts elaborated in our previous publications,[1] we have successfully synthesized several novel Fe-based bulk metallic glasses (BMGs) which can be cast to fully glassy rods with diameters up to 12 mm.[2] In this talk, we will present the experimental results of these newly developed BMGs, together with the alloy design schemes, origins of the high GFA and implications of this study. Our work also demonstrated that minor additions of adequate elements are very powerful in designing new BMGs with superior GFA. This research was sponsored by the Division of Materials Sciences and Engineering, Office of Basic Energy Sciences, U.S. Department of Energy under contract DE-AC05-00OR-22725 with UT-Battelle, LLC. [1]Z. P. Lu & C. T. Liu, Phys. Rev. Lett., 91(2003)115505. [2]Z. P. Lu & C. T. Liu, Phys. Rev. Lett., 92(2004)245503.

9:35 AM
In Situ Synchrotron Study of Multiscale Phase Transformations in Bulk Metallic Glass: *Jonathan Almer*[1]; Xun-Li Wang[2]; Alexandru D. Stoica[2]; Ling Yang[4]; C. T. Liu[4]; [1]Argonne National Laboratory, Advd. Photon Source, 9700 S. Cass Ave., Bldg. 431, Argonne, IL 60439 USA; [2]Oak Ridge National Laboratory, Spallation Neutron Source, Oak Ridge, TN USA; [4]Oak Ridge National Laboratory, Metals & Ceram. Div., Oak Ridg, TN USA; [4]University of Cincinnati, Cheml. & Matls. Engrg., Cincinnati, OH USA

We report on in situ measurements of wide-angle x-ray scattering (WAXS) and small-angle x-ray scattering (SAXS) during annealing of Zr-based bulk metallic glasses. The combination of WAXS and SAXS permits material investigation over length scales ranging from Angstroms to microns, respectively. Measurements were carried out at Sector1 of the Advanced Photon Source, using E=80keV x-rays. Such high-energy x-rays offer penetration comparable to neutrons, ensuring that the probe volume is bulk-representative, and provide access to a large volume of reciprocal space. By using an undulator and specialized optics, coupled with area detectors, we demonstrate temporal resolutions on the order of 15 seconds, sufficient for kinetic observations. We find that phase transformations proceed in stages, with distinctively different kinetics. Nanometer sized clusters form first, as revealed by SAXS, followed by an abrupt amorphous-to-crystalline phase transformation, as revealed by WAXS. These results are compared with complementary DSC measurements, and related to transformation theory.

9:55 AM
Role of Ti Replacement for Zr in the Formation of ZrTiCuNiAl Bulk Metallic Glasses: *D. Ma*[1]; *H. Cao*[1]; L. Ding[1]; K. C. Hsieh[2]; Y. Austin Chang[1]; [1]University of Wisconsin, Dept. of Matls. Sci. & Engrg., 1509 Univ. Ave., Madison, WI 53706 USA; [2]Sun Yat Sen University, Inst. of Matls. Sci. & Engrg., Kaohsiung, Taiwan 80424 Taiwan

We present a series of ZrTiCuNiAl alloys, which can readily form glassy rods with at least 2 mm in diameter using a conventional copper-mould casting method. Replacement of Zr with Ti, while maintaining the compositions of the other elements constant, appears to decrease the glass-forming abilities (GFA), which eventually vanished at a critical Ti content of 7 at%. To gain an understanding of the GFA of these alloys, we calculated a temperature versus Ti composition section, or an isopleth, using our thermodynamic description recently developed. These thermodynamic calculations suggest that bulk glass formation of these alloys are associated with the suppression of an invariant eutectic reaction, i.e., L —> Cu2TiZr + t3_AlCuZr + NiZr + Cu10Zr7 + AlCu2Zr. The decrease in the GFA with the replacement of Zr by Ti could be attributed to increasing liquidus temperatures as well as competition between the formation of glassy and crystalline phases.

10:15 AM Break

10:35 AM
On the Origin of High Glass Forming Ability in Bulk Metallic Glasses: *Ralf Busch*[1]; [1]Oregon State University, Dept. of Mechl. Engrg., 204 Rogers Hall, Corvallis, OR 97331 USA

Bulk metallic glass forming liquids are alloys with typically three to five elemental components that have a large size mismatch.[1] They are dense liquids with small free volumes and viscosities that are several orders of magnitude higher than in pure metals or known alloys. In addition these melts are energetically closer to the crystal than other metallic melts due to their high packing density in conjunction with a tendency to develop short range order. These factors lead to slow crystallization kinetics. The crystallization kinetics is very complex especially in the vicinity of the glass transition due to the influence of phase separation and the decoupling of the diffusion constants of the different species. Recent developments, such as shear rate depend viscosity are discussed. [1]R. Busch, JOM-J Min. Met. Mat. S. 52, 39 (2000).

10:55 AM
Thermodynamics and Kinetics of Complex Liquids: Bulk Metallic Glass: *Hans J. Fecht*[1]; Rainer Wunderlich[1]; Guojiang Fan[2]; [1]University of Ulm, Dept. of Matls., Faculty of Engrg., Albert-Einstein-Allee 47, Ulm D-89081 Germany; [2]University of California, Cheml. Engrg. & Matls. Sci., One Shields Ave., Davis, CA 95616 USA

With complex alloys forming BMG crystallization can be avoided over a broad temperature/time window. As such, the relevant thermodynamic properties of the metastable glassy and undercooled liquid state can be directly measured below and above the glass transition temperature before crystallization on a nanometer scale sets in. The results for various thermodynamic functions, such as S(T), H(T), G(T) and V(T) together with the measurement of the viscosity (T) give new insight into the nature of the highly undercooled liquid state and the glass transition itself. The results on Zr-Ti-Ni-Cu-Be and Pd-Ni-Cu-P melts suggest a scenario where the glass transition in a metallic alloy is not a phase transition in the classical sense but kinetic freezing triggered by an underlying entropic instability. Further results are discussed within the framework of a new fragility concept. The financial support by the European Space Agency ESA (ThermoLab program MAP) is gratefully acknowledged.

11:15 AM
Atomic Size Effects on Glass Formability: *Mo Li*[1]; Payman Jalali[1]; [1]Georgia Institute of Technology, Sch. of Matls. Sci. & Engrg., 771 Ferst Dr., Atlanta, GA 30332 USA

Effects of atomic size difference on glass formability is investigated in this work using both numerical simulations and analytical approaches. In a model system where atomic size effects are separated from other factors such as enthalpy of formation, we found that atomic size difference plays a role in kinetics for various competing phases, including glass. It is the competition of these different kinetic processes that eventuall leads to glass formation in the system which has longer times for crystallization.

11:35 AM
Thermodynamics and Kinetics of Pd43Ni10Cu27P20 Bulk Metallic Glass-Forming Liquid: *Guojiang Fan*[1]; H. Choo[1]; P. K. Liaw[1]; H. J. Fecht[2]; [1]University of Tennessee, Matls. Sci. & Engrg., Dougherty Engrg. Bldg., Knoxville, TN 37996 USA; [2]University of Ulm, Matls. Div., Ulm 89081 Germany

Recently, several families of multicomponent alloys with a complex chemistry show a much sluggish kinetics for the crystal nucleation during undercooling, which enables the formation of bulk metallic glasses (BMGs) at relatively slow cooling rates. In order to gain an insight on the BMGs formation and also develop BMGs with new compositions, it is essential to understand the thermodynamics and kinetics of bulk metallic glass-forming liquids, which dominate the glass formation. In this study, the thermodynamics and kinetics of the Pd43Ni10Cu27P20 bulk metallic glass-forming liquid have been investigated over a wide temperature range. The thermodynamic functions for this liquid have been calculated, based on the measured specific heat capacity for the liquid and crystal as well as the enthalpy of fusion. The fragility of the Pd43Ni10Cu27P20 bulk metallic glass-forming liquid has been determined, which indicates that this liquid is relatively fragile, despite the best glass-forming ability found thus far. The excellent glass-forming ability of this alloy is attributed to a smaller thermodynamic driving force and larger diffusion length for crystallization than in other bulk-metallic-glass-forming alloys.

Carbon Technology: Anode Raw Materials

Sponsored by: Light Metals Division, LMD-Aluminum Committee
Program Organizers: Todd W. Dixon, ConocoPhillips, Borger, TX 79007 USA; Halvor Kvande, Norsk Hydro ASA, Oslo N-0240 Norway; Markus Meier, R&D Carbon, Sierre CH 3960 Switzerland

Monday AM Room: 2007
February 14, 2005 Location: Moscone West Convention Center

Session Chairs: Bruce Goddard, ConocoPhillips, Ponca City, OK 74602-1267 USA; Todd W. Dixon, ConocoPhillips, Borger, TX 79007 USA

8:30 AM
Characterization of Reactivity of Green and Calcined Petcoke with Oxygen for Application to Combustion Systems: *Constance L. Senior*[1]; David O. Lignell[1]; Zumao Chen[1]; Adel F. Sarofim[1]; Todd W. Dixon[2]; [1]Reaction Engineering International, 77 W. 200 S., Ste. 210, Salt Lake City, UT 84101 USA; [2]ConocoPhillips, Borger Refinery, Spur 119 N., Borger, TX 79007 USA

Petcoke combustion differs from coal combustion because of the inherent properties of the fuel. The lower volatile content of petcoke and the lower surface area of the char relative to coal make petcoke more difficult to ignite than coal and require longer burnout times relative to coal. Green cokes generally have volatile matter in the range of 8-10%, whereas calcined cokes have on the order of 1% volatile matter. Measurements of green petcoke reactivity have not been previously reported in the literature, particularly measurements made at the high temperatures characteristic of a flame. This paper presents information on petcoke combustion kinetics that was obtained from combustion of coke samples under well-controlled conditions. Green petcoke reactivity was higher than that of calcined coke, but lower than coal. Measured reactivities were used to model the combustion of petcoke and to explore the effects of particle size and temperature on burnout time.

8:55 AM
Comparison of Physical Properties of Finer Grains of Calcined Cokes Generated During Calcination with Those Originally Present in Green Cokes: *Ravindra Narayan Narvekar*[1]; [1]Goa Carbon Limited, Production, Dempo House, Campal, Panaji, Goa 403001 India

Green coke is an aggregate of various grain sizes ranging from few microns to few inches.The finer particles present in green cokes are more susceptible to burn inside the kiln or get drifted outside the kiln alongwith combustion gases.Simultaneously finer particles are generated inside the kiln during the calcination process because of intense heat and abrasion during transportation from feed end to discharge end of the kiln.Now Goa Carbon Limited has tried to find out whether rrrrrthe generated finer grains of calcined coke differ from originally present finer grains in physical characteristics.There are indications that the generated finer grains are significantly denser than originally present finer grains as seen from bulk density,apparent density etc.

9:20 AM
A Tool for Predicting Anode Performance of Non-Traditional Calcined Cokes: *Keith J. Neyrey*[1]; Les Edwards[1]; J. Anthony Ross[2]; Franz Vogt[1]; [1]CII Carbon, LLC, Techl., 1615 E. Judge Perez, 4th Fl., Chalmette, LA 70043 USA; [2]Century Aluminum of WV, Inc., PO Box 98, Ravenswood, WV 26164 USA

The supply of traditional calcinable green coke is not meeting demand, which has resulted in calciners using green cokes that are typically sold to the fuel market. In order for calciners to more thoroughly evaluate non-traditional cokes (higher sulfur and metals and higher volatile content), a simple microscopic method was developed to make an empirical determination of coke quality. Microscopic analysis of calcined coke is not a new technique, and many papers have been published on the subject. Sophisticated software and equipment have been developed to perform such analyses. The simpler method used in this study is economically feasible for a production laboratory. The paper describes the microscopic analysis of a number of traditional and non-traditional cokes. Bench scale anodes were prepared and evaluated for critical properties. These properties were correlated to the results of the microscopic evaluations and other common coke quality measures. Comments about the performance of these cokes in anodes are given.

9:45 AM
Multivariate SPC Applications in the Calcining Business: *Michael Marcon*[1]; Todd W. Dixon[2]; Arvin Paul[3]; [1]InControl Technologies, Inc., 3845 FM, 1960 W. Ste. 318, Houston, TX 77068 USA; [2]ConocoPhillips, Borger Refinery, Spur 119 N., Borger, TX 79007 USA; [3]ConocoPhillips, Lake Charles Calcining Plant, PO Box 3187, Lake Charles, LA 70602-3187 USA

The introduction of Advanced Process Control (APC) has changed the way process engineers view the operating principals of industrial control schemes. While the major benefit of APC is to provide tighter control by reducing control variable variation, one of the side benefits of APC is they collect data on all phases of the operation. A tool to extract additional information from the available data and further reduce the operational region is multivariate statistical process control (MVSPC). This is a statistical procedure based on the correlations that exists between the process variables. By taking advantage of these correlations, it is possible to maintain production within this multivariate region and further reduce overall variation and lower production cost. Advanced statistical analysis of a commercial, rotary kiln can provide a useful, quantitative measure of process stability and, more importantly, allow on-line fault detection of process control elements.

10:10 AM Break

10:25 AM
Physical Characterization and Reactivity Measurerments of Anode Butt Cores: *John Marthin Andresen*[1]; [1]Pennsylvania State University, The Energy Inst., 407 Academic Activities Bldg., State College, PA 16802 USA

The recycling of anode butt material is frequently used improve the economics of the Hall-Héroult process, where alumina is reduced by carbon to produce aluminum. Since about 15-30wt% of a new anode can consist of recycled butt material this fraction could have a significant impact on the performance of the new anode in the bath. However, very little is known about the variation in anode butt materials chemistry where major differences can have been developed during electrolysis. On one hand, the lower part has been in contact with the hot electrolyte experiencing temperatures in the range of 930 to 980°C and may also have been modified by CO2 burn where typically the binder coke is attacked selectively. On the other hand, the top part of the anode reaches a temperature in the range of 350 to 600°C depending on the protective cover of electrolyte material and air burn may take place. Further, the middle part of the anode butt may not be affected by any of the above. This work focuses on the variation of physical properties of anode butt cores using non-destructive and destructive methods. X-ray computed tomography scanning was used as a non-destructive method to study the overall structure of the anode butt cores from the air burn side to the work face. Parallel to the non-destructive study, conventional destructive data, including apparent and absolute densities, and specific pore volume, were obtained for the anode butt cores representing different position in the reducing pot. The data indicate that the carbon near the air-burn side as well as that of the working face have somewhat higher porosity than the center of the core, that may lead to higher reactivity.

10:50 AM
Studying Mesophase Contents in Pitches from Different Sources: *A. S. Tayanchin*[1]; Y. D. Kratzova[2]; V. S. Biront[2]; J. A. Johnson[1]; [1]RUSAL Engineering and Technological Center, Krasnoyarsk Russia; [2]Krasnoyarsk University of Non-Ferrous Metals and Gold, Krasnoyarsk Russia

The ultimate goal for the present work was to study the pitch anisotropic content and liquid/solid phase formation in different Russian pitch supplies and to identify and compare the contents of fine anisotropic inclusions and mesophase areas. The study showed that mesophase contents and sizes of mesophase areas have reasonable correlation with the pitch softening point whereas the probability of mesophase generation increases with the increase in softening point. Mesophase content is minimal in the as produced pitches. However, an intensive ordering of structures in the pitch, which is associated with the growth of mesophase spheroids, starts at the pitch temperatures in the range of 420-450°C. Several consecutive “coke over coke” phases have been identified for creation of mesophase starting from nucleation, growth of mesophase spheroid that further coalescences into the mesophase package (particle). Correlations have been established between mesophase and size of the mesophase areas.

11:15 AM
Procedure for Testing Infiltration Property of Pitches: *V. K. Frizorger*[1]; Y. D. Kratzova[2]; A. S. Tayanchin[1]; [1]RUSAL Engineering

and Technological Center, Krasnoyarsk Russia; [2]Krasnoyarsk University of Non-Ferrous Metals and Gold, Krasnoyarsk Russia

A simple test procedure was developed for testing pitch infiltration (pitch wetting) in to the coke, which is based on using pencils of pitch specifically made for the tests. The test procedure avoids some of the issues with existing pitch wetting procedures related to the time consumed in the test, degree of variation of test results and sensitivity to even minor changes in the experimental lay-out. The test procedure looks for the coefficient of pitch infiltration which is not dependent on such factors as the mass of pitch or coke, the shape or size of the pitch or coke and it eliminates the influence of the test container material with the coke and pitch placed for experiments. The procedure is highly sensitive to changes in the pitch properties and the resultant rate of pitch infiltration into the coke is independent of the coke and pitch properties.

Cast Shop Technology: Cast Shop Safety

Sponsored by: Light Metals Division, LMD-Aluminum Committee
Program Organizers: Gerd Ulrich Gruen, Hydro Aluminium AS, Bonn 53117 Germany; Corleen Chesonis, Alcoa Inc., Alcoa Technical Center, Alcoa Center, PA 15069 USA; Halvor Kvande, Norsk Hydro ASA, Oslo N-0240 Norway

Monday AM Room: 2001
February 14, 2005 Location: Moscone West Convention Center

Session Chair: Seymour G. Epstein, The Aluminum Association Inc, Washington, DC 20006 USA

8:30 AM
A Summary of Findings from Twenty Years of Molten Metal Incident Reporting: *Seymour G. Epstein*[1]; [1]The Aluminum Association, Inc., 900 19th St. NW, Ste. 300, Washington, DC 20006 USA

For more than 50 years the aluminum industry has had an ongoing effort to gain an understanding of molten aluminum-water explosions and how they may be prevented. In spite of these extensive efforts, explosions continue to occur. Following the occurrence of several devastating explosions in the early 1980s, The Aluminum Association established a formal world-wide program of reporting molten metal incidents to enhance awareness, to complement the industry's research efforts and to provide guidance for the Association's safety efforts. Much has been learned from this program, and the findings from 20 years of reporting will be summarized in this paper.

8:55 AM
Scrap Melting Safety - Improving, But Not Enough: M. D. Bertram[2]; *F. R. Hubbard*[2]; D. C. Pierce[1]; [1]Consultant, 8408 Twin Lake Ct., Richmond, VA 23229 USA; [2]IMCO Recycling, 397 Black Hollow Rd., Rockwood, TN 37854 USA

Over the years scrap suppliers and processors have learned many lessons about improving safety in melting operations. Most plant personnel are aware of the typical hazards involved in melting scrap aluminum. However, there are issues that challenge the best efforts of management to keep their plants and people safe. Tightening scrap supplies, small items that create large problems (e.g., air bag cylinders) and very dense scrap containing contaminants are three issues that can make safety a challenge in the melting facility. Equipment upgrades plus continued education/training and communication help, but the fact that serious molten metal incidents continue to occur, prove that there is a need for additional vigilance in this arena.

9:20 AM
Safe Charging of RSI (Remelt Secondary Ingot) and Other Ingot Shapes into Melting Furnaces: *John L. Zeh*[1]; [1]Logan Aluminum Inc., U.S. Hwy. 431 N., Russellville, KY 42276 USA

Safety is the first requirement when charging a melting furnace. Moisture and other contaminants have repeatedly shown that their presence on or in RSI or other charge materials can cause catastrophic explosions. Logan Aluminum Inc. is one of the largest users of RSI thus has extensive experience in safe use of this material. Other charge materials such as magnesium and magnesium alloy ingot present similar dangers. Steps to ensure safe use of sows or ingots include communication to suppliers of safety requirements, incoming material specifications, inspection and test, quarantine and rejection procedures, safe pre-melting processing (drying, storage and inventory tracking) and melt furnace charging. This system significantly reduces the risk of explosion during melting.

9:45 AM
Cause and Prevention of Explosions Involving DC & EMC Casting of Aluminum Sheet Ingot: *Ray T. Richter*[1]; J. Martin Ekenes[2]; [1]Alcoa Inc., Alcoa Techl. Ctr., Alcoa Ctr., PA 15069 USA; [2]Hydro Aluminum

The casting of aluminum alloy sheet ingot and T-bar presents the potential for some of the most volatile situations that can occur in DC (direct chill) and EMC (Electromagnetic) casting processes. Aluminum Association explosion incident data from over 300 explosions spanning a period of more than twenty years was reviewed and analyzed looking for common factors and repetitive reasons for explosions. Analysis of explosions occurring during the three stages of sheet ingot casting, 'start of cast', 'steady state' and 'end of cast', were examined and prioritized. Case studies illustrate the need for understanding both technical and non-technical factors contributing to explosions involving molten metal. This paper identifies the major causes of explosions involving DC casting of aluminum alloy sheet ingot and makes recommendations for how to prevent the recurrence of such events and minimize the risk of injury.

10:10 AM Break

10:20 AM
A Safe Cast Abort System for D.C. Sheet Ingot with Non-Tilting Furnaces: *John A. Paris*[1]; Michael J. Matisko[1]; [1]Alcoa Inc., 4879 State St., Bettendorf, IA 52722 USA

During DC casting operations, emergency situations arise that require the ability to safely terminate the casting operation when the trough and filtering systems are full of metal from furnace to casting table. Safe termination includes stopping the platen and draining away the metal without putting personnel at risk to injury. Older casting facilities often do not have the systems and equipment capable of performing a safe termination and space is generally very limited. A forty-year old DC casting pit at Alcoa Davenport Works was modified to provide this capability. This paper discusses the design criteria, space and equipment constraints, and procedural changes that resulted in a successful retrofit to allow safe casting aborts on this older DC casting station.

10:45 AM
Preventing Molten Metal Explosions Related to Skim Tools and Salt: *Edward M. Williams*[1]; Ray T. Richter[2]; Donald L. Stewart[2]; Jake J. Niedling[3]; [1]Alcoa Inc, Hwy. 66, PO Box 10, Newburgh, IN 47629 USA; [2]Alcoa Inc, Alcoa Techl. Ctr., Alcoa Ctr., PA 15069 USA; [3]Alcoa Inc, 900 S. Gay St., Riverview Tower, Knoxville, TN 37902 USA

In 2003, Alcoa Inc. experienced a number of molten aluminum explosions that were associated with skim tools used for cleaning in-line metal treatment units. These explosions were investigated and the incidents appeared to be related to the residual skim and dross on the tools from previous skimming operations. Visual observations indicated high moisture content on the skim left on the tools once they cooled to room temperature. Analysis of the dross confirmed that it contained varying amounts of magnesium chloride salts, which are highly hygroscopic at room temperature. Testing was performed analyzing the skim and investigating moisture pick-up and release during cooling and heating cycles. Based upon this analysis procedural and equipment modifications were made to minimize the risk of further explosions.

11:10 AM
Casthouse Safety - A Focus on Dust: *David D. Leon*[1]; [1]Alcoa Inc., Alcoa Techl. Ctr., Alcoa Ctr., PA 15069 USA

Information, training and safeguards regarding aluminum dusts and their explosibility has traditionally focused on pure metallic powders, pigments, pastes, and their associated handling facilities. But incidents throughout the aluminum industry has shown that there are hidden dangers in other processes, like casting and metal fabricating, which can generate potentially explosive dusts. This paper will introduce the audience to the hazards associated with potentially explosive dusts, where they can be found in the casthouse, prevention methods, and actions to be taken in case of an incident.

11:35 AM Panel Discussion

Characterization of Minerals, Metals and Materials: Extraction and Processing Applications

Sponsored by: Extraction & Processing Division, EPD-Materials Characterization Committee
Program Organizers: Tzong T. Chen, Natural Resources Canada, CANMET, Ottawa, Ontario K1A 0G1 Canada; Ann M. Hagni, Construction Technology Laboratories, Inc., Microscopy Group, Skokie, IL 60077 USA; J. Y. Hwang, Michigan Technological University, Institute of Materials Processing, Houghton, MI 49931-1295 USA

Monday AM Room: 2010
February 14, 2005 Location: Moscone West Convention Center

Session Chairs: Tzong T. Chen, Natural Resources Canada, CANMET, Ottawa, Ontario K1A 0G1 Canada; John E. Dutrizac, Natural Resources Canada, CANMET, Ottawa, Ontario K1A 0G1 Canada

8:30 AM Invited
Formation of Mg-Al Layered Double Hydroxide Modified by Organic Acid Anions and its Application to Wastewater Treatment: *Tomohito Kameda*[1]; Masami Saito[2]; Shingo Saito[2]; Yoshiaki Umetsu[1]; [1]Tohoku University, IMRAM, 1,1 Katahira 2-Chome, Aoba-ku, Sendai 980-8577 Japan; [2]Tohoku University, Dept. of Applied Chmst., Grad. Sch. of Engrg., Aoba 07, Aoba-ku, Sendai 980-8579 Japan

Development of scavengers to remove heavy metal ions and organic pollutants from wastewaters has been attempted by coupling Mg-Al layered double hydroxide (Mg-Al LDH) with organic acid anions having functional groups in their structure, such as EDTA and organic sulfonic acid. These organic-modified Mg-Al LDHs were synthesized by adding a solution of magnesium and aluminum nitrates to alkaline solution containing the organic acid anion. The solid product was confirmed to be hydrotalcite-like compounds with Al/Mg mole ratio of 1/3 and to have intercalated organic anions in the interlayers. The EDTA-modified Mg-Al LDH was found to remove rapidly Cu2+ and Cd2+ from aqueous solution. The organic sulfonate-modified Mg-Al LDH could uptake organic pollutant exampled by bisphenol A. This organic sulfonate-modified Mg-Al LDH was regenerated by extraction of the uptaken organic pollutant with ethanol, and confirmed to have a high potentiality for the repeated use.

8:55 AM Invited
Characterization of Iron(III) Oxyhydroxides in Hydrometallurgical Residues: *Mitch Loan*[1]; William Richmond[2]; Tim St. Pierre[3]; Gordon M. Parkinson[2]; [1]University of Limerick, Matls. & Surface Sci. Inst., Limerick Ireland; [2]Curtin University of Technology, AJ Parker CRC for Hydrometall., Nanochmst. Rsch. Inst., GPO Box U 1987, Perth, W.A. 6845 Australia; [3]University of Western Australia, Sch. of Physics, Mailbag Delivery Point M013, Crawley, Perth, W.A. 6009 Australia

The characterization of iron(III) oxyhydroxides in hydrometallurgical residues can be a complicated task. Iron-phases in residues commonly arise after neutralization and precipitation of liquors to remove dissolved iron or after addition of soluble iron to remove dissolved impurities. Iron-phases also precipitate in storage ponds, mine drainage and waste streams where air or bacteria oxidize dissolved Fe(II). The low solubility of iron creates a high supersaturation environment favouring the formation of nanoscale and metastable phases. These phases often have poor physical properties and contain high loadings of adsorbed components - often the element being refined. Importantly, low proportions of iron(III) oxyhydroxides (~ 20 wt%) can still control the physical properties of a residue, and also release adsorbed toxins on transformation to more crystalline phases. In this study, the application of multiple techniques to differentiate among the various iron(III) oxyhydroxide phases, and the complications involved in characterizing the poorly crystalline ferrihydrite, schwertmannite, akaganeite and goethite in a heterogeneous sample environment are demonstrated.

9:20 AM Invited
Influence of Platinum Group Metals Mineralogy on their Leachability During a Chloride-Assisted Pressure Oxidation Process: *C. Joe Ferron*[1]; C. C. Hamilton[1]; O. Valeyev[1]; N. Davidson[1]; [1]SGS Lakefield Research Limited, Metallurgl. Tech., PO Box 4300, 185 Concession St., Lakefield, Ontario K0L 2H0 Canada

The PLATSOL process was developed to extract simultaneously, base metals, gold and platinum group metals from various materials. Extensive research has indicated that most PGM's were amenable to the PLATSOL process, with the notable exception of cooperite PtS. Further work showed that a thermal pretreatment at 500-700ºC transformed the structure of the cooperite and similar refractory minerals (Pt, Pd) S into Pt metal and Pt-Pd alloys that responded very well to the PLATSOL process. Examples are presented of the mineralogy of PGM concentrates as produced, in the residue from the PLATSOL leach and after pre-treatment.

9:45 AM
Storing Capacity of Copper Ions in Vermiculite and Its Relations to the Preparation Conditions: *Bowen Li*[1]; *Janny-Yang Hwang*[1]; Shuhui Yu[2]; [1]Michigan Technological University, Inst. of Matls. Procg., 1400 Townsend Dr., Houghton, MI 49931 USA; [2]China University of Geosciences, Matl. Dept., 29 Xueyuan Rd., Beijing, Beijing 100083 China

The storing capacity of copper ion in vermiculite was investigated and its relations to the preparation conditions were determined based on the ion exchange reaction between vermiculite and copper chloride solution. The factors that effecting the carrying capacity of vermiculite with copper ions, such as particle size of vermiculite, concentration of the copper ion in the solution, pH value, reaction temperature and reaction time, etc. were investigated individually. The best reaction condition for preparing Cu-vermiculite is 0.1M copper ion concentration, pH 3.0, 80-90°C reaction temperature and 3 hours reaction time. The Cu-vermiculite carrying 5.5wt% copper was prepared with vermiculite powder of 4.1 microns in average diameter.

10:10 AM Break

10:20 AM Invited
Developing an Atomic-Level Understanding of the Mechanisms that Govern CO2 Mineral Carbonation Reaction Processes: *Michael J. McKelvy*[1]; Andrew V.G. Chizmeshya[1]; Jason Diefenbacher[2]; Hamdallah Béarat[2]; R. W. Carpenter[1]; George Wolf[3]; [1]Arizona State University, Ctr. for Solid State Sci., Sci. & Engrg. of Matls. Grad. Prog., Tempe, AZ 85287 USA; [2]Arizona State University, Ctr. for Solid State Sci., Tempe, AZ 85287 USA; [3]Arizona State University, Dept. of Chmst. & Biochmst., Tempe, AZ 85287 USA

Mineral carbonation is an intriguing CO2 sequestration candidate technology, which produces environmentally benign and geologically stable materials. The primary challenge is economically viable process development. Serpentine and olivine minerals are exciting candidate feedstock materials, due to their wide availability, low-cost, and rapid mineral carbonation potential. Cost-effectively enhancing their carbonation rate is critical to reducing mineral sequestration process cost. We will discuss our recent research into the mechanisms that govern serpentine/olivine mineral carbonation reaction processes, including in situ observations of the mineral carbonation process and a novel mechanistic approach to enhance carbonation reactivity that avoids the cost of mineral activation. Our goal is to develop the necessary atomic-level understanding to engineer improved carbonation materials and processes to reduce process cost.

10:50 AM Invited
Alkaline Leaching for Mixture of Nickel Hydroxide and Nickel-Rare Earth Alloy: *Masao Miyake*[1]; Masafumi Maeda[1]; [1]University of Tokyo, Inst. of Industl. Sci., Internatl. Rsch. Ctr. for Sustainable Matls., 4-6-1 Komaba, Meguro, Tokyo 153-8505 Japan

A leaching treatment was investigated to recover metals including rare earths from the mixture of Ni hydroxide and hydrogen storage alloy. By leaching with an ammoniacal alkaline aqueous solution, only Ni hydroxide was dissolved from the mixture and the hydrogen storage alloy could be recovered without decomposing. The effects of leaching conditions such as pH and temperature on the dissolution rate of Ni hydroxide were examined.

11:15 AM Invited
Development and Application of Laser Ablation Microprobe (LAM)-ICP-MS for Analysis of Trace Precious Metals: *Louis J. Cabri*[1]; Paul J. Sylvester[2]; Mike N. Tubrett[2]; Anna Peregoedova[3]; Greg McMahon[4]; J.H. Gilles Laflamme[5]; [1]Cabri Consulting Inc., 99 Fifth Ave., Ste. 122, Ottawa, Ontario K1S 5P5 Canada; [2]Memorial University of Newfoundland, Dept. of Earth Scis., St. John's, Newfoundland A1B 3X5 Canada; [3]McGill University, Dept. of Earth & Planetary Scis., 3450 Univ. St., Montreal, Quebec H3A 2A7 Canada; [4]Fibics Incorporated, 556 Booth St., Ste. 200, Ottawa, Ontario K1A 0G1 Canada; [5]CANMET, MMSL, 555 Booth St., Ottawa, Ontario K1A 0G1 Canada

In-situ analyses of trace precious metals at low levels (10s to 100s of ppb) are important for quantifying mineralogical balances and for solving process problems when used together with detailed mineralogical study. This will be a focus of academic research and contractual work for industry in the new Inco Innovation Centre located at Memorial University of Newfoundland. Sulfide standards were developed and tested for LAM-ICP-MS analyses of potential precious metals carriers in sulfides (e.g. pentlandite, pyrite, pyrrhotite, and chalcopyrite). After use of sintered single-element platinum-group element (PGE) and Au standards (Ballhaus & Sylvester, 2000) and fused FeS single-PGE standards (Cabri et al., 2003), we have successfully characterized fused FeS standards containing six PGE+Au and applied them in several projects ranging from determination of PGE partitioning in experimental sulfide charges (Mungall et al., in press) to exploration samples and process products for mass balance calculations.

Computational Aspects of Mechanical Properties of Materials: Atomistic Methods

Sponsored by: Materials Processing and Manufacturing Division, MPMD-Computational Materials Science & Engineering-(Jt. ASM-MSCTS)

Program Organizers: Kwai S. Chan, Southwest Research Institute, Department of Materials Science, San Antonio, TX 78284 USA; Diana Farkas, Virginia Polytechnic Institute and State University, Department of Materials Science and Engineering, Blacksburg, VA 24061 USA

Monday AM Room: 3012
February 14, 2005 Location: Moscone West Convention Center

Session Chairs: Christopher Woodward, Air Force Research Laboratory, MLLMD, Dayton, OH 45433 USA; Vaclav Vitek, University of Pennsylvania, Matls. Sci. & Engrg., Philadelphia, PA 19104 USA

8:30 AM Invited
Modeling Nanoscale Elastic Instabilities: *Krystyn J. Van Vliet*[1]; [1]MIT, DMSE, 77 Mass. Ave., Rm. 8-214, Cambridge, MA 02139 USA

Computational modeling of inelastic deformation is complicated by the range of length and timescales involved in nucleation, motion and interaction of defects such as dislocations in crystalline materials. Here, we present a computational approach that combines the atomistic detail of molecular dynamics with the large structural length scale of continuum models. We find that the application of this atomistically informed continuum approach is well-suited to the study of elastic instabilities in crystals, in particular under concentrated surface loads as typical of nanoindentation. With this computational tool, we consider the effects of microstructural and macrostructural dimensions on the elastic limit of crystals and crystalline structures of nanoscale physical dimensions.

9:05 AM
Ab-Initio Computational Calculations of Elastic Constants of Titanium Boride (TiB) Using Density Functional Theory: *K. S. Ravi Chandran*[1]; Krutibas Panda[1]; [1]University of Utah, Metallurgl. Engrg., # 412, 135 S., 1460 E., Salt Lake City, UT 84112 USA

Ab-initio computational calculations of anisotropic elastic constants of titanium boride, TiB have been performed using the computational implementation of Density Functional Theory (DFT) in Wien2k. TiB has orthorhombic crystal structure, thus nine independent elastic constants are to be determined to completely understand its elastic behavior. TiB has attracted attention as reinforcement in metal matrix composites, wear resistance coating and monolithic ceramic due to its high hardness and elastic modulus. The elastic constants were determined using the Full-Potential Linearized Augmented-Plane-Wave (FLAPW) method with the generalized gradient approximation (GGA) by employing specific distortions of the unit cell. The single crystal elastic constants were determined using both the unrelaxed and relaxed atomic positions. It has been found that relaxation has significant effect on the single crystal elastic constants. The nature of chemical bonding and electronic charge transfer in TiB has been studied to provide insight into its superior mechanical properties such as high hardness and high stiffness values.

9:25 AM
Bond-Order Potentials for Magnetic Transition Metals: Application to Defect Behaviour in Iron: *Duc Manh Nguyen*[1]; Guo Qiang Liu[2]; David G. Pettifor[3]; [1]UKAEA Fusion, Theory & Modlg., Culham Sci. Ctr., Abingdon, Oxfordshire OX14 3DB UK; [2]Chinese Academy of Science, Inst. of Physics, PO Box 603, Beijing 100080 China; [3]University of Oxford, Dept. of Matls., Parks Rd., Oxford, Oxfordshire OX1 3PH UK

Ferritic steels are the prime candidate materials for structural components of future fusion power plants. The development of genetic methods for modelling iron-based alloys under neutron irradiation is an issue of significant importance for the international fusion programme. The conventional molecular dynamic treatments of transition metals involve embedded atom models or Finnis-Sinclair potentials. However, ferromagnetic properties of iron are poorly described by such central force schemes, because the stability of the bcc crystal structure arises from magnetic effects, which in turn depend on local environments. In this talk, a robust and real space tight-binding bond-order potential is formulated for transition metal alloys by including both directional bonding and magnetism to describe accurately the complexities introduced by ferromagnetism. Physical properties are determined self-consistently within the Stoner model of band magnetism. The constructed BOP was applied in modelling point defects with special focus on magnetic and energetic properties of different interstitial configuration.

9:45 AM
Molecular Dynamics Study of Mutli-Cycle Single Asperity Contact: *Jun Song*[1]; Pil-Ryung Cha[2]; David J. Srolovitz[1]; [1]Princeton University, Dept. of Mechl. & Aeros. Engrg., Bowen Hall, 70 Prospect Ave., Princeton, NJ 08540 USA; [2]Kookmin University, Sch. of Metallurgl. & Matls. Engrg., 861-1, Chongnung-Dong, Songbuk-Gu, Seoul 136-702 Korea

Many MEMS devices employ mechanical contacts as high frequency electrical switches. These contacts occur on the nano- and micro-scales. Elastic/plastic deformation, adhesion and morphology evolution all play important roles in the operation of these devices. We perform a molecular dynamics simulation of single asperity (EAM) Au contacts under cyclic loading and unloading. We monitor the full force-displacement curve, the evolution of the atomic structure/asperity morphology, dislocation nucleation and motion. We correlate features in the force-displacement relation to both dislocation motion and morphology evolution. One common feature of the simulations is the transfer of atoms from one side of the asperity contact to the other. The material transport is related to both adhesion and plastic deformation. We separate these effects by modify the interatomic potential to controllably reduce adhesion.

10:05 AM
Impurity Effects on Grain Boundary Fracture at the Atomic Scale: *Diana Farkas*[1]; Brian Hyde[1]; Margarita Ruda[2]; [1]Virginia Tech, Dept. of Matls. Sci., 201 Holden Hall, Blacksburg, VA 24060-0237 USA; [2]Centro Atomico Bariloche, Bariloche Argentina

We investigate the mechanisms of fracture behavior in bi-crystals and nano-crystalline bcc Fe at the atomic scale using empirical force laws and molecular level simulations. The simulations are focused on modeling how the presence of interstitial impurities affects the behavior of grain boundaries during fracture. The results show that C interstitial impurities strengthen the grain boundaries in both bi-crystals and the nano-crystalline material, inhibiting grain boundary failure. For very small grain sizes, the presence of interstitial C also inhibits the process of grain boundary sliding. H impurities, on the other hand, strongly promote grain boundary fracture in bi-crystals.

10:25 AM Break

10:35 AM Invited
Smoothed Atom Mechanics: A Meshless Quasicontinuum: *Ronald E. Miller*[1]; Ellad Tadmor[2]; [1]Carleton University, Mech. & Aero. Engrg., 1125 Col. By Dr., Ottawa, ON K1S 5B6 Canada; [2]Technion, Mechl. Engrg., Technion City, Haifa 32000 Israel

The Quasicontinuum (QC) method is a multiscale technique based on the idea of representative atoms and finite element interpolation, which greatly reduces the number of required degrees of freedom in an atomistic problem without significant loss of accuracy. The method offers a seamless transition from fully-atomistic regions to coarsened continuum regions by changing the density of atoms visited in the calculation, i.e. the representative atoms. The QC method has been very successful in treating two-dimensional (2D) problems, however when extended to three dimensions (3D) it is found that the gain in degree-of-freedom reduction can sometimes be offset by the cost of the 3D meshing associated with the finite element interpolation. This is a significant shortcoming, since most problems of interest in atomic-scale mechanics are 3D in nature. In this talk, we introduce a reformulation of the QC method within a meshless framework using the recently developed "local optimal point interpolation" (LOPI) scheme. We refer to the new approach as Smoothed Atom Mechanics (SAM) to

highlight its connection with smoothed particle hydrodynamics. SAM provides a more natural framework than QC for adaptive refining and coarsening of the model. In 3D, it is significantly faster than QC due to the elimination of the need for mesh generation. It is also a framework that can be easily and efficiently parallelized. Details of the new formulation will be presented, along with preliminary examples that highlight the capabilities of the method.

11:10 AM Invited
Dislocation Structure, Phase Stability and Yield Stress Behavior of Platinum Group $L1_2$ Intermetallics: Combined Ab-Initio-Peierls-Nabarro Model Approach: *Oleg Y. Kontsevoi*[1]; Yuri N. Gornostyrev[1]; Arthur J. Freeman[1]; [1]Northwestern University, Physics & Astron., 2145 N. Sheridan Rd., Evanston, IL 60201 USA

The dislocation structure and mobility are among the key phenomena governing the deformation and fracture behavior of intermetallic alloys. We present the results of fundamental comparative studies of the dislocation properties and the mechanical behavior for a class of intermetallic alloys based on platinum group metals (PGM) which are being developed for ultra-high temperature applications: Ir_3X and Rh_3X (where X = Ti, Zr, Hf, V, Nb, Ta). To connect the microscopic and mesoscopic scales in the analysis of dislocation structure and mobility, we employ a combined approach based on highly accurate first-principles calculations of the shear energetics and the modified semi-discrete 2D Peierls-Nabarro model with an ab-initio parametrization of the restoring forces. Based on our analysis of dislocation structure and mobility, we provide predictions of temperature yield stress behavior of PGM-based intermetallics, show that their dislocation properties are closely connected with the features of electronic structure and $L1_2$ -> $D0_{19}$ structural stability, and demonstrate the dramatic difference in dislocation structure and the mechanical behavior between PGM alloys with IVA and VA group elements. Supported by the AFOSR (grant No. F49620-01-1-0166).

11:45 AM
Atomistic Predictions of Non-Planar Dislocation Core Structures in fcc Iridium Using Bond-Order Potentials with Greens Function Boundary Conditions: *Marc J. Cawkwell*[1]; Duc Nguyen-Manh[2]; David G. Pettifor[3]; Vaclav Vitek[1]; [1]University of Pennsylvania, Dept. of Matls. Sci. & Engrg., 3231 Walnut St., Philadelphia, PA 19104 USA; [2]UKAEA Fusion, Culham Sci. Ctr., Abingdon OX14 3DB UK; [3]University of Oxford, Dept. of Matls., Parks Rd., Oxford OX1 3PH UK

Iridium is a promising material for use in aggressive environments due to its corrosion resistance and high melting temperature. However, unlike any other fcc metal, it can undergo brittle transgranular cleavage at temperatures up to 500°C, the origin of which is likely hidden in the atomic level properties of dislocations. We have developed Bond-Order Potentials for atomistic simulation of extended defects in iridium that are an excellent description of cohesion. Simulation of the core structure of the screw dislocation in iridium using Greens function boundary conditions has highlighted two possible configurations; a planar core dissociated into Shockley partials and a metastable non-planar core spreading into intersecting {111} planes. We have evaluated the Peierls stress of these configurations and suggest the limited mobility of the non-planar core could contribute to the strong work hardening and brittle cleavage of iridium. Research supported by the DOE BES grant. No. DE-PG02-98ER45702 (MJC, VV).

12:05 PM
Yield Criterion for Plastic Flow in Body-Centered Cubic Metals Based on Atomistic Modeling of Glide of Screw Dislocations: *Roman Gröger*[1]; Vaclav Vitek[1]; Vikranth Racherla[2]; John L. Bassani[2]; Luzhong Yin[3]; [1]University of Pennsylvania, Dept. of Matls. Sci. & Engrg., 3231 Walnut St., Philadelphia, PA 19104 USA; [2]University of Pennsylvania, Dept. of Mechl. Engrg. & Applied Mech., 297 Towne Bldg., 220 S. 33rd St., Philadelphia, PA 19104 USA; [3]Rensselaer Polytechnic Institute, Scientific Computation Rsch. Ctr., 110 8th St., CII-7013, Troy, NY 12180 USA

Plastic deformation of body-centered cubic (bcc) metals is controlled by the glide of a/2<111> screw dislocations owing to their low mobility resulting from non-planar cores. Upon loading such cores transform and become asymmetric which is responsible for complex asymmetries and orientation dependencies of the yield and flow stress. In order to elucidate these phenomena we performed molecular statics modeling of the motion of an a/2[111] screw dislocation in bcc molybdenum loaded by combination of shear stresses perpendicular and parallel to the Burgers vector. While shear stresses perpendicular to the slip direction cannot induce glide, they alter the core structure and affect significantly the glide process. Based on these results, we have formulated a general yield criterion that includes both shear stresses parallel and perpendicular to the slip direction. This criterion is verified by comparing its predictions with experimental observations of slip traces in single crystals of molybdenum at low temperatures.

12:25 PM
Solid-Solution Softening Trends in BCC Mo by First Principles: *Dallas R. Trinkle*[1]; Richard G. Hennig[2]; Thomas J. Lenosky[2]; Satish Rao[1]; Christopher Woodward[1]; [1]Air Force Research Laboratory, MLLMD, Bldg. 655, 2230 10th St., Wright Patterson AFB, OH 45433-7817 USA; [2]Ohio State University, Dept. of Physics, 174 W. 18th Ave., Columbus, OH 43210 USA

Solid solution softening observed in the group VA and group VIA transition metals has traditionally been attributed to either extrinsic—such as interstitial scavanging—or intrinsic—direct solute/dislocation interaction—effects. We investigate intrinsic mechanisms using first principles methods. First, density functional theory calculates the change in the primary Peierls barrier when Re, Hf, Os, W, Ir and Pt solutes are introduced along a straight a/2<111> screw dislocation in Mo. Here the local strain field associated with the dislocation core is self-consistently coupled to the long-range elastic field using the recently developed lattice Greens Function Boundary Condition method. We compare with classical solute potential results and the work of Fleischer to understand the effect of size and modulus misfit on softening in bcc transition metals. The connection of classical potentials with ab initio data allows the extension of chemically accurate calculations to physically relevant length scales.

Computational Thermodynamics and Phase Transformations: Grain Boundaries and Interfaces I

Sponsored by: Electronic, Magnetic & Photonic Materials Division, Materials Processing & Manufacturing Division, Structural Materials Division, EMPMD/SMD-Chemistry & Physics of Materials Committee, MPMD-Computational Materials Science & Engineering-(Jt. ASM-MSCTS)
Program Organizers: Corbett C. Battaile, Sandia National Laboratories, Materials and Process Modeling Department, Albuquerque, NM 87185-1411 USA; Christopher Mark Wolverton, Ford Motor Company, Scientific Research Laboratory, Dearborn, MI 48121-2053 USA

Monday AM Room: 3005
February 14, 2005 Location: Moscone West Convention Center

Session Chair: Corbett C. Battaile, Sandia National Laboratories, Matls. & Process Modlg. Dept., Albuquerque, NM 87185-1411 USA

8:30 AM Keynote
Anisotropic Grain Boundary Properties: *David J. Srolovitz*[1]; Hao Zhang[1]; Mikhail I. Mendelev[1]; [1]Princeton University, Mechl. & Aeros. Engrg., Princeton, NJ 08540 USA

Grain boundary structure and properties depend on five distinct crystallographic variables: three to describe the relative orientation of one grain with respect to the other and two to describe the boundary plane. The evolution of polycrystalline structures may depend upon the anisotropy in grain boundary mobility, grain boundary free energy/stiffness, efficiency with which the boundary absorbs defects. In this presentation, we focus upon grain boundary properties that are important for quantitative modeling of the evolution of polycrystalline microstructures as a function of these crystallographic parameters (i.e., grain boundary mobility and grain boundary stiffness). We discuss how to determine these properties using molecular dynamics simulations. Finally, we compare predicted grain boundary dynamical properties with experimental measurements to draw some conclusions on what controls the rate at which polycrystalline structures evolve.

9:15 AM Invited
Grain Boundary Energy Anisotropy: Modeling and Implications: *James A. Warren*[1]; [1]National Institute of Standards and Technology, Metall./CTCMS, 100 Bureau Dr., Stop 8554, Gaithersburg, MD 20899 USA

The excess free energy associated with a grain boundary depends on both the misorientation and the inclination of the plane between the bounding grains. In two dimensions two parameters are required to specify the energy, while in three dimensions five are required. Here we explore several methods for incorporating this anisotropy into a phase field model of grain boundaries, explore the physical consequences of each approach, compare analytic models with MD simulations, and examine the implications in modeling the dynamics of grain rotation.

9:45 AM
Dependence of Grain Boundary Mobility on Boundary Plane: *Hao Zhang*[1]; Mikhail I. Mendelev[1]; David J. Srolovitz[1]; [1]Princeton University, Dept. of Mechl. & Aeros. Engrg., Bowen Hall, 70 Prospect Ave., Princeton, NJ 08540 USA

Quantitative grain boundary mobility data is a pre-requisite for quantitative predictions of such microstructural processes as grain growth and recrystallization. Such data has never been determined experimentally or via simulation as a function of boundary plane. We present the results of a series of 3-d molecular dynamics simulations in which the grain boundary mobility was determined as a function of boundary plane and temperature. Elastic strains are used to drive the motion of a series of nominally flat Sigma5 <001> tilt grain boundaries in Ni. We also determine the activation energies for boundary migration and compare how they vary with boundary plane with similar data on self-diffusion along the same grain boundaries. This similarity in the data provides some hints to the basic mechanism of grain boundary migration.

10:05 AM
An Atomistic Study of Grain Boundary Wetting: *Ho-Seok Nam*[1]; Mikhail I. Mendelev[1]; David J. Srolovitz[1]; [1]Princeton University, Dept. of Mechl. & Aeros. Engrg., 70 Prospect Ave., Princeton, NJ 08544 USA

There are many examples in which a liquid metal in contact with a polycrystalline solid of a different composition develops a deep liquid groove at the intersections of the grain boundaries and the solid-liquid interface. In many cases, the liquid film quickly penetrates into the solid along the grain boundary. The rate of propagation of such liquid layers can be greatly accelerated by the application of even modest stresses. This is a form of liquid metal embrittlement. We have performed a series of molecular dynamics simulations using a set of binary embedded atom method potentials that can be adjusted to vary the thermodynamic properties of the system. We report on how the liquid films propagate as a function of temperature, solubility, melting point difference and grain boundary character. These results are compared with general trends gleaned from a series of experimental studies in the literature.

10:25 AM Break

10:40 AM Invited
On Computer Simulations of Zener Pinning: *Mark Andrew Miodownik*[1]; Azmir Harun[1]; Mike Clode[1]; Elizabeth Ann Holm[2]; [1]King's College London, Mechl. Engrg., Strand, London WC2R 2LS UK; [2]Sandia National Laboratories, Matls. & Process Modlg., Albuquerque, NM USA

Zener pinning is an enigmatic phenomenon that has so far resisted a complete theoretical understanding due its inherent multi-scale complexities. In this talk we briefly review the successes and failures of the different theoretical approaches to understanding this phenomenon. We the present new work which compares the ability of three different types of microstructural model to simulate Zener pinning: The Phase Field model, the Front Tracking model and the Monte Carlo Potts model. The same 3D test geometry is simulated using each method. This is an hexagonal network with spherical particles located at the centre of each hexagonal grain. The hexagonal grain network provides a constant driving force for a moving boundary and includes triple line and quadruple point motion. This geometry allows detailed investigation of the boundary/particle interaction. The shape of the boundaries during bypass are compared with theoretical predictions and previous simulations. The pinning force acting on the migrating curved grain boundary is also calculated and compared with theoretical predictions for each model. The advantages and disadvantages of each type of model are highlighted. The ability of the models to simulate the pinning force of non-spherical and incoherant particles is also discussed.

11:10 AM Invited
Insights from Large Scale Modeling of Grain Growth Including Misorientation Dependent Boundary Mobility and Diffusive Solute Drag: *Koenraad G.F. Janssens*[1]; Elizabeth A. Holm[1]; [1]Sandia National Laboratories, PO Box 5800, MS 1411, Albuquerque, NM 87111 USA

In technical materials, grain growth is a microstructure transformation process of high complexity. The evolution of its statistically relevant quantities, such grain size, shape and (mis-)orientation distribution, is highly dependent on locally interdependent variables, such as grain boundary energy and mobility and local solute activity. Adding to the complexity, phenomena like anomalous grain growth may be determined by processes with a low occurrence probability (e.g. 1 in 100000 grains). This fact makes large-scale simulations of the evolution of a large number of grains of interest. We will present the development and applications of a massive-parallel-type, irregular, shapeless cellular automata based computational model for grain growth including crystallography and solute drag. Results provide insight into the collective nature of the grain growth process. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under Contract DE-AC04-94AL85000.

11:40 AM
Effects of Fe and Mg Co-Segregation on Boundary Migration in Al: *Mikhail I. Mendelev*[1]; David J. Srolovitz[1]; [1]Ames Laboratory, Ames, IA 50011 USA

Even small concentrations of impurities can dramatically modify the mobility of grain boundaries in otherwise pure metal. Analytical models describing this effect consider only one type of impurities while real materials contain several different impurities. We developed an extension of the Cahn-Lucke-Detert continuum model for the case in which a material contains two types of impurities. In order to apply this analytical model to the case of Al containing Fe and Mg as impurities, we need to know the grain boundary mobility in pure Al, the Fe and Mg diffusivities and their heats of segregations to a grain boundary in Al. These data are obtained from molecular dynamics simulation. The interatomic potentials are fit to a wide range of crystal, liquid and defect properties in Al-Fe and Al-Mg alloys. Using these data we predict the dependence of the grain boundary mobility on Mg concentration in Al sample which already contains small amount of Fe impurities.

12:00 PM
Diffusion Mechanism at the Grain Boundaries in Two-Dimensional Metals: Gennady Mikhailovich Poletaev[1]; Roman Juryevich Rakitin[1]; *Mikhail Dmitrievich Starostenkov*[1]; [1]Altai State Technical University, Gen. Physics Dept., Lenin st., 46, Barnaul 656038 Russia

The present paper is concerned with the research of diffusion mechanism at the grain boundaries in two-dimensional metals by the method of molecular dynamics. The diffusion of atoms was studied on the example of three metals: Ni, Al, Cu. The packing of two-dimensional crystals was corresponded to the plane [111] of FCC lattice. The researches were made, using two types of the potentials of interatomic interaction: Morse pair potentials and multipartial Finnis-Sinclair potentials. The mechanism, the dependences of the coefficient of diffusion at the grain boundaries in the dependence on temperature, mutual orientation of grains, free volume, energy of grain boundaries were studied. It was found, that leading diffusion mechanism at the lowangle grain boundaries of two-dimensional metals was the result of interaction of grain boundary dislocation pairs. The creep of dislocation pairs in opposite sides was observed in the experiments.

Converter and Fire Refining Practices: Plenary

Sponsored by: Extraction & Processing Division, EPD-Pyrometallurgy Committee
Program Organizer: Alistair G. Ross, INCO, Ltd., Canadian Smelting & Copper Business, Copper Cliff, P0M 1N0 ON Canada

Monday AM Room: 2016
February 14, 2005 Location: Moscone West Convention Center

Session Chairs: Alistair G. Ross, Inco Ltd, Canadian Smelting & Copper Business, Copper Cliff, ON P0M 1N0 Canada; Tony Eltringham, BHP Billiton, Houston, TX 77056-3020 USA

8:30 AM Opening Comments

8:45 AM
Progress in Converting and Casting: *Theo Lehner*[1]; *Alistair G. Ross*[3]; [1]New Boliden, Rönnskar Smelter and Lulea University of Technology, Sweden; [3]Inco Ltd, Copper Cliff Ops., 18 Rink St., Copper Cliff, ON P0M 1NO Canada

Turning matte into anodes continues to be an area to watch: for visitors to see pyrometallurgy in action; for metallurgists to keep up with modern smelting furnaces and ever increasing production rates; for management to remain profitable using more tools than taught in school; and for environmentalists to detect the last small clouds from the ever cleaner smelter. Current converting practices have been screened and analyzed, and today, converting and casting is a modern industry. An impressive, though typical learning curve of converter productivity may be detected. Local conditions such as availability and type of raw materials, products extracted, cost factors, etc., have stimulated the development of add-ons or even alternatives to the still

dominant method of converting by Peirce-Smith technology. Turning blister copper into anodes follows a similar path, namely increased productivity and improved quality. We dare to predict that development will continue.

9:15 AM
Recent Developments on the Peirce-Smith Converting Process at the Rönnskär Smelter: *Magnus Ek*[1]; *Peter Olsson*[1]; [1]New Boliden, Smelter Operations, Se-932 81, Skelleftehamn Sweden

After the installation of three new converters as part of the recent expansion of the Rönnskär smelter completed in 2000 work continues to further improve the converter operation. The converter upgrade led to an increase in blister copper taps from 150 tons per batch to more than 300 tons. The total cathode copper production increased from 130,000 tons in 1999 to 230,000 tons in 2001, the first year in full production. In recent years focus has been to improve operating practice, maximize the blowing time, extend the converter campaigns hence to reduce the specific brick consumption and improve the converter slag composition.

9:45 AM
Developments in Peirce-Smith Converting at Inco's Copper Cliff Smelter During the Past 35 Years: *Tony Warner*[1]; Jin Liu[1]; Frank Javor[2]; Randy Lawson[2]; Warren Shellshear[2]; Tien V. Hoang[2]; Ron Falcioni[2]; [1]Inco Technical Services Limited, 2060 Flavelle Blvd., Sheridan Park, Mississauga, Ontario L5K 1Z9 Canada; [2]Inco Limited, Copper Cliff Smelter, Copper Cliff, Ontario P0M 1N0 Canada

At the Copper Cliff Smelter, Inco Limited has extensive experience in converting primary smelting mattes over a broad range of nickel/copper ratios and compositions. Over the past 35 years, technology developments at Inco have reduced the number of Peirce-Smith converters in Nickel/Bulk service from thirteen to five. This paper will discuss; the performance and operating life of "stretch" 13.7 m. vessels compared to conventional 10.7 m. converters; process control and information system development from the early 1980's, to monitor converter aisle status on a continuous basis, to the recent central control of the "stretch" converters; nitrogen cooling of "finishing" matte, from plant testing to implementation in the early 1990's, to replace the dedicated cooling converters; the impact on converting due to changes in the smelter flow sheet in the early 1990's; as well as a review of a current program, under consideration, to develop a future converting strategy to address environmental issues and smelter profitability.

10:15 AM Break

10:30 AM
Control and Optimization of Converting Practices: *Florian Kongoli*[1]; Ian McBow[1]; Robert Budd[2]; S. Llubani[1]; [1]FLOGEN Technologies Inc., Metals Dept., 5757 Decelles Ave. # 511, Montreal, QC H3S 2C3 Canada; [2]FLOGEN Technologies Inc., 3422 Old Capitol Trail, #791, Wilmington, DE 19808 USA

Converters have been playing an important role in the extraction and processing of metals ever since the first type of converter was invented about 100 years ago. Historically their operation has been mainly based on the experience of talented operators rather than on strict control and optimization technologies. However, in the new realities of unavoidable necessity to increase productivity and in the conditions of diversification of primary materials from various geographical areas, improving control and optimization techniques have become indispensable. In this paper a review of the authors' previous work in terms of improving control and optimization of converter operational practices related to magnetite content and precipitation, slag and metal blows, problematic and dangerous elements such as As, Sb etc. has been described by highlighting the advantages that the new control and optimization methods and tools bring to everyday converter practices. Several examples are given and future work is underlined.

11:00 AM
High Oxygen Shrouded Injection at Falconbridge: 5 Years of Operation: *Joel P. Kapusta*[1]; *Hans Strickling*[2]; William Tai[2]; [1]Air Liquide Canada Inc., 90, Boul. Marie-Victorin, Boucherville, Québec J4B 1V6 Canada; [2]Falconbridge Limited, Falconbridge, Ontario P0M 1S0 Canada

Although Peirce-Smith converting remains the workhorse in matte converting, the copper and nickel industries are still confronted with production hindrances such as tuyere blockage, excessive refractory wear and limits in the oxygen enrichment levels of the blast air. The knowledge acquired on high-pressure gas injection technology as well as the invention of the concentric tuyere for steelmaking led to the development of the Air Liquide Shrouded Injector (ALSI) technology for copper and nickel converting. Following a technology demonstration in 1997-98 with four shrouded injectors installed in a Peirce-Smith converter, Falconbridge Limited implemented ALSI Technology on a commercial scale in May 1999 as an integral part of its new Slag Make Converter at Sudbury, Ontario, Canada. The paper presents the various aspects of commissioning ALSI Technology, as well as the operating changes and injector design modifications over the five years the shrouded injectors have been in operation.

11:30 AM
Improving Inco's MK Reactor Performance Through Application of Praxair's Coherent Jet (CoJet) Technology: Tony Warner[1]; *Jin Liu*[1]; Dave McCann[2]; Dave E. Hall[2]; Dave Malette[2]; Jennifer A. Bradley[2]; Eric Mackenzie[3]; Adrian Deneys[4]; [1]Inco Technical Services Limited, 2060 Flavelle Blvd., Sheridan Park, Mississauga, Ontario L5K 1Z9 Canada; [2]Inco Limited, Copper Business, Copper Cliff Smelter, Copper Cliff, Ontario P0M 1N0 Canada; [3]Praxair Canada Inc., 1 City Centre Dr., Ste. 1200, Mississauga, Ontario L5B 1M2 Canada; [4]Praxair Metals Technologies, 1500 Polco St., Indianapolis, IN 46224 USA

A novel low-pressure adaptation of Praxair's coherent jet technology, utilizing "CoJet" lances, was developed for application at Inco's Copper Cliff Smelter where oxygen is available in large tonnage quantities, but only at relatively low supply pressures (< 28 psig header pressure). The project objectives were to evaluate the effect of coherent jet technology on controlling accretion formation at the tip of the oxygen lance and also to increase the oxygen utilization efficiency in the Inco "Oxygen Top-Blowing Nitrogen Bottom-Stirring" (TBBS) MK Reactor, used for converting nickel-contaminated chalcocite to semi-blister copper. This paper describes the development and subsequent implementation and testing of two CoJet lances in this application.

Corrosion Sensors and Monitoring

Sponsored by: Structural Materials Division, SMD-Corrosion and Environmental Effects Committee-(Jt. ASM-MSCTS)
Program Organizers: James C. Earthman, University of California, Department of Chemical and Materials Science, Irvine, CA 92697-2575 USA; Raúl B. Rebak, Lawrence Livermore National Laboratory, Livermore, CA 94550 USA

Monday AM Room: 3018
February 14, 2005 Location: Moscone West Convention Center

Session Chair: Raúl B. Rebak, Lawrence Livermore National Laboratory, Livermore, CA 94550 USA

8:30 AM
Microelectromechanical Systems (MEMS) for Detecting Corrosion: *Mario H. Castro-Cedeno*[1]; [1]Rochester Institute of Technology, Mfg. & Mechl. Engrg. Tech., 78 Lomb Memorial Dr., Rochester, NY 14623-5604 USA

Microelectromechanical systems (MEMS) are devices that extend integrated circuits (IC) technology by adding sensing elements and/or actuators to the silicon chip. The goals are a complete system on a chip and significant reductions in system size, weight and cost. MEMS are ideal for detecting and monitoring corrosion because they enable real-time health monitoring of structures or components under operational conditions. They can use well-known techniques for detecting corrosion such as linear polarization resistance, acoustical noise and electrochemical measurements. In this paper, examples of MEMS sensors for corrosion detection and monitoring are proposed and test results of a prototype device based on linear polarization resistance are presented.

9:00 AM
Electrochemical Characterization of Nanocrystalline Surface of Alloy 22: *Krishnan Selva Raja*[1]; Manoranjan Misra[1]; Shantanu A. Namjoshi[1]; [1]University of Nevada, Metallurgl. & Matls. Engrg., 1661 N. Virginia St., MS 388, Reno, NV 89557 USA

A nano-crystalline surface with well defined grain size of less than 20 nm could be achieved by localized surface deformation followed by a low temperature annealing. This paper will discuss the processing steps of creating an optimized nano-crystalline surface layer on Alloy-22, a Ni-Cr-Mo-W alloy. Preliminary studies of surface modification of Alloy 22 by conventional shot peening followed by annealing at 300-350°C for 1-2 h showed improved passivity and increased charge density of the passive film. Scanning Kelvin Probe studies are being carried out to investigate the potential gradients across the passive

films of nano-crystalline surface. Results of these studies coupled with TEM analyses will help understand the underlying mechanism for improved corrosion resistance of nano-structured surface.

9:30 AM
Monitoring the Evolution of the Corrosion Potential and Corrosion Rate of Alloy 22 Immersed in Various Electrolyte Solutions: John C. Estill[1]; Gary A. Hust[1]; Kenneth J. King[1]; *Raul B. Rebak*[1]; [1]Lawrence Livermore National Laboratory, 7000 East Ave., L-631, Livermore, CA 94550 USA

Alloy 22 (N06022) is a Nickel-Chromium-Molybdenum (Ni-Cr-Mo) alloy, which has excellent general and localized corrosion resistance. Depending on the exposed electrolyte composition and temperature, the corrosion potential (Ecorr) of Alloy 22 may gradually increase as the time increases. The raise in Ecorr (ennoblement) is generally accompanied by a reduction in the corrosion rate, suggesting the formation of a protective oxide film on the alloy surface. Results are presented to show the correlation between Ecorr and the corrosion rate in various electrolyte solutions and temperatures. Studied variables included ratio of chloride to nitrate, pH and creviced vs. non-creviced testing specimens.

10:00 AM Break

10:15 AM
Early Corrosion Detection by Magnetoelastic Techniques and Electrochemical Impedance Spectroscopy: Francisco Rumiche[1]; Alberto Polar[1]; Varsha Singh[1]; George M. Lloyd[1]; Ming L. Wang[1]; *J. Ernesto Indacochea*[1]; [1]University of Illinois, Dept. of Civil & Matls. Engrg., 842 W. Taylor St., MC 246, Chicago, IL 60607 USA

A sensor based on magnetoelastic techniques was developed as a nondestructive technique to detect early corrosion in carbon steel cables and tendons used in stay bridges and reinforcements. The magnetic response in terms of the effect of corrosion on conductivity and permeability of the material was monitored by adjusting the input current signal to localize the induced magnetic field in a depth between 0.01 and 1.5 mm. Conventional electrochemical techniques and Electrochemical Impedance Spectroscopy were used to follow the development and establish the early stages of corrosion. The results of these techniques were correlated to the measurements of the magnetoelastic sensor. Furthermore, optical microscopy, X-Ray analysis, electron scanning microscopy with the electron dispersion spectroscopy probe and Raman spectroscopy were used to characterize systematically the passive films and corrosion products correlating the results with the measurements of the magnetic response of the surface of the carbon steel specimens.

10:45 AM
The Use of Electrochemical Impedance Spectroscopy (EIS) to Measure the Corrosion of Metals in Contact with Wood: *Samuel L. Zelinka*[1]; Douglas R. Rammer[1]; [1]USDA Forest Products Laboratory, Condition Assessment & Rehabilitation of Struct., 1 Gifford Pinchot Dr., Madison, WI 53726 USA

Recent replacement of traditional preservative treatments with newer, more corrosive chloride based preservatives highlight the ineffectiveness of current fasteners to resist corrosion and the need for tools to predict the service life (durability) of a bare or coated fastener in preservative treated wood. One possible technique to quantify the increased corrosivity of the new preservative treatments is use of Electrochemical Impedance Spectroscopy (EIS). EIS is well suited to measuring the corrosion in wood because it can be used in situ, works well in high resistance media, and does not permanently polarize the ions in the wood. While EIS is used to measure corrosion in other materials, this technique has not been developed for the wood environment. We will present preliminary results on the utilization of EIS to measure the corrosion rate of metals in wood.

11:15 AM
Corrosion Monitoring in Kraft Digesters with EN Probes: *Steven J. Pawel*[1]; [1]Oak Ridge National Laboratory, 1 Bethel Valley Rd., Bldg. 4500-S, MS-6156, Oak Ridge, TN 37831 USA

Electrochemical noise (EN) probes were deployed in two continuous kraft digesters at a variety of locations representative of corrosion throughout the vessels. Current and potential noise, the temperature at each probe location, and the value of up to 60 process parameters (flow rates, bulk liquor chemistry, etc.) were monitored continuously during each experiment. The results indicate that changes in furnish composition and process upsets were invariably associated with concurrent substantial changes in EN activity throughout the vessels. Post-test evaluation of the mild steel electrode materials in both vessels confirmed general corrosion of a magnitude consistent with historical trends in the respective vessels as well as values qualitatively (and semi-quantitatively) related to EN current sums for each electrode pair. Stainless steel electrodes representing 309LSi and 312 overlay repairs exhibited zero wastage corrosion - as did the actual overlays - but the EN data indicated periodic redox activity on the stainless steel that varied with time and position within the vessel. Little or no correlation between EN probe activity and other operational variables was observed in either vessel.

Extractive Metallurgy: Pyrometallurgy I

Sponsored by: Extraction & Processing Division, EPD-Aqueous Processing Committee, EPD-Pyrometallurgy Committee, EPD-Waste Treatment & Minimization Committee
Program Organizers: Thomas P. Battle, DuPont Titanium Technologies, Wilmington, DE 19880-0352 USA; Edgar E. Vidal, Colorado School of Mines, Golden, CO 80401-1887 USA; Courtney A. Young, Montana Tech of the University of Montana, Metallurgical Engineering, Butte, MT 59701 USA

Monday AM — Room: 2018
February 14, 2005 — Location: Moscone West Convention Center

Session Chairs: Edgar E. Vidal, Colorado School of Mines, Metall. & Matls. Engrg., Golden, CO 80401 USA; Tom Battle, DuPont Titanium Technologies, Wilmington, DE 19880-0352 USA

8:30 AM
Separation of Al_2O_3 Inclusions Across Interfaces Between Molten Steel and Ladle-, Tundish- and Mold-Slags: *George N. Shannon*[1]; S. Sridhar[1]; [1]Carnegie Mellon University, Dept. of Matls. Sci., 5000 Forbes Ave., Pittsburgh, PA 15213 USA

The modeling of inclusions separating across a steel-slag interface previously introduced by Nakajima/Okamura and Bouris/Bergeles is expanded to include different inclusions shapes (octahedral and plate-like, besides spherical) as well as comparison between model ladle-, tundish-, and mold-slags. Investigation of the relation of these shapes with the interfacial capillary force - which arises due to the dynamic interfacial energy during separation - has shown that the force has a significant effect on whether the inclusion separates rapidly or settles at the interface. For the slags considered, the most significant physical property is found to be viscosity, which results in fast separation and dissolution times for the mold and ladle slags, relative to the more viscous tundish slag. Particle dissolution (using experimental data) is included in separation modeling. Deformable inclusions are also discussed, wherein the shape-change force deflects some of the inclusion's inherent driving force to separate.

9:00 AM
Process for Converting SO_2 to Sulfur Without Generating Pollutants Through Reactions Involving BaS and $BaSO_4$: *Hong Yong Sohn*[1]; Marijanka Savic[1]; Rafael Padilla[2]; Gilsoo Han[1]; [1]University of Utah, Metallurgl. Engrg., 135 S. 1460 E., Rm. 412, Salt Lake City, UT 84112-0114 USA; [2]University of Concepcion, Dept. of Metallurgl. Engrg., Concepcion, Chile

Nonferrous smelters and coal gasification processes generate sulfur dioxide streams, most of which are treated to produce sulfuric acid with the accompanying problems of market shortage and transportation difficulties. A method for converting sulfur dioxide to elemental sulfur by a cyclic process involving barium sulfide and barium sulfate without generating solid wastes has been developed. In this process, barium sulfate is reduced by a suitable reducing agent such as hydrogen to produce barium sulfide, which is used to reduce sulfur dioxide and produce elemental sulfur vapor and regenerate barium sulfate. The latter is then reduced to reproduce barium sulfide. Thermodynamic analysis and experimental results indicated that the BaS-SO_2 reaction produces mainly sulfur vapor and solid barium sulfate and that the gaseous product from the $BaSO_4$-H_2 reaction is mainly water vapor. The rates of the two reactions are reasonably rapid in the temperature range 700-1050°C.

9:30 AM
A Thermodynamic Model of Combustion Zone in Lead Blast Furnace: *Pengfu Tan*[1]; Pierre Vix[1]; [1]Mount Isa Mines Limited, Metallurgl. Plants Bldg., Private Mail Bag 6, Mt. Isa, Queensland 4825 Australia

A thermodynamic model has been developed to model the distribution behaviors of Cu, Fe, S, O, Pb, Zn, As, and heat balance in lead blast furnace. The model results have been validated by the industrial data of Kazzinc in Kazakhstan. It can be predicted for any set of controllable

process parameters such as feed composition, smelting temperature, degree of oxygen enrichment and volume of oxygen-enriched air. The effects of the blast air, industrial oxygen, and coke charge on the distributions of Cu, Fe, S, O, Pb, Zn, As, and heat balance, and lead loss in slag have been presented and discussed.

10:00 AM Break

10:15 AM Cancelled
The Interaction of a Highly Soluble Gas Jet and a Liquid

10:45 AM
Preparation of Magnesium Oxide with Low Calcium Oxide Content and High Specific Surface Area from Low-Grade Dolomite: *Xiang-Yang Zhou*[1]; *Jie Li*[1]; *Hong-Zhuan Liu*[1]; *Ye-Xiang Liu*[1]; [1]Central South University, Sch. of Metallurgl. Sci. & Engrg., Changsha, Hunan 410083 China

The low energy consumption preparation technology of magnesium oxide with low calcium oxide content and high specific surface area from low-grade dolomite has been investigated. The better magnesium oxide preparation technology conditions are the followings: (1)dolomite powder is partially calcined at 750-800°C for 2h, (2) solid-liquid ratio in calcined dolomite slurry should be 20~30g/l, (3) carbonation temperature, carbon pressure and carbonation time are less than 40°C,0.4~0.6Mpa and 1.5~2h respectively during carbonation process, (4) decomposition temperature of Mg(HCO3)2 solution should be more than 90°C, (5) calcination temperature of precursor is less than 850. More than 90% of magnesium can be extracted by the technology. The MgO product (CaO<0.38%) with a specific surface area of near 50m2-g-1 also can be obtained by the technology.

11:15 AM
Further Improvements and Applications of the Altair Hydrochloride Pigment Process: *Dirk Verhulst*[1]; Bruce J. Sabacky[1]; Bob Wang[1]; Douglas K. Ellsworth[1]; [1]Altair Nanomaterials, Inc., 204 Edison Way, Reno, NV 89502 USA

Altair owns a 5 t/day-feed pilot plant for the processing of ilmenite ores. It involves digestion in concentrated hydrochloric acid, solvent extraction to concentrate Ti in a purified stream, and spray hydrolysis to produce, after calcination and milling, a high quality pigment. All chloride streams are recycled. Our latest work includes a systematic study of the solvent extraction step via small-scale tests and modelization. Feedstocks other than ilmenite ores are also being explored. We are working on the treatment of oil sand tailings for the recovery of Ti and Zr and on supplying electrodes for the manufacture of Ti metal by molten salt electrolysis.

Friction Stir Welding and Processing III: Aluminum Alloys

Sponsored by: Materials Processing & Manufacturing Division, MPMD-Shaping and Forming Committee
Program Organizers: Kumar V. Jata, Air Force Research Laboratory, Materials & Manufacturing Directorate, WPAFB, OH 45433 USA; Thomas J. Lienert, Los Alamos National Laboratory, Los Alamos, NM 87545 USA; Murray W. Mahoney, Rockwell Science Center, Thousand Oaks, CA 91360 USA; Rajiv S. Mishra, University of Missouri, Metallurgical Engineering, Rolla, MO 65409-0340 USA

Monday AM Room: Nob Hill C/D
February 14, 2005 Location: San Francisco Marriott

Session Chair: Kumar V. Jata, Air Force Research Laboratory, WPAFB, OH 45433 USA

8:30 AM Welcome/Opening Remarks

8:40 AM Keynote
Commercialization of Friction Stir Welding - A Lab to Production Success Story: *Doug Waldron*[1]; Keith McTernan[1]; [1]Advanced Joining Technologies, 3030 Red Hill Ave., Santa Ana, CA USA

While the benefits of friction stir welding (FSW) have been widely published since 1995, demonstrations of its end use in production applications have been limited. This paper will present several examples of production transitions within several market sectors such as aerospace, marine, transportation (road), oil and gas, and extrusions. Further, the process of transitioning from research studies to production applications will be presented. Examples of product implementation begin with the first successful implementation of FSW into aerospace on The Boeing Company's Delta launch vehicle program to the first US marine implementation in both commercial and military market vessels. Transportation applications will also be discussed illustrating a high volume application potential supported by the FSW process. This paper provides an overview on a typical FSW project lifecycle that includes process development, mechanical testing, certification issues, and an economic business case for production implementation.

9:00 AM
Microcharacterization and Texture Analysis of Friction Stir Processed AA 5052 Alloy: *Michelle N. Adams-Hughes*[1]; Peter N. Kalu[1]; Marwan K. Khraisheh[2]; Namas Chandra[1]; [1]FAMU- FSU College of Engineering, Mechl. Engrg., 2020 Pottsdamer Rd., Rm. 229, Tallahassee, FL 32310 USA; [2]University of Kentucky, Mechl. Engrg., 210C Ctr. for Robotics & Mfg. Sys., Lexington, KY 40506- 0108 USA

Friction Stir Processing (FSP) was employed in the fabrication of AA 5052 alloy (0.11 Si, 0.25 Fe, 0.17 Cu, 0.03 Mn, 2.2 Mg, 0.25 Cr, 0.02 Zn, balance Al - all compositions are in wt.%). The material was characterized using, SEM, OIM and X-Ray diffraction. A correlation was made between the processing parameters (rotation and translation speeds) and the microstructure and the texture developed in the material. The rotation speed had a greater effect on the development of the microstructure than the translation speed. Lower rotation speed resulted in a finer grain size. The grain orientation, average grain misorientation, and grain misorientation spread for each processing condition is presented in this paper.

9:30 AM Invited
Influence of Thermal Environments on Friction Stir Welding Operating Windows: *R. J. Lederich*[1]; J. A. Baumann[1]; [1]The Boeing Company, PO Box 516, MC S245-1003, St. Louis, MO 63166-0516 USA

Successful FSW requires maintenance of the appropriate hot working temperature range and sufficient forging force for the duration of the weld. For a given FSW tool and weld setup (parts to be welded, anvil, and clamps), temperature is determined by the spindle speed (rpm), travel speed (ipm), and to a lesser extent, the forging force. We have produced lap welds joining 3.2 mm (0.125") thick 2024Al sheets to substrate configurations having widely different heat conduction characteristics. Temperatures were measured by installing thermocouples at identical locations along the length of the weld. We have determined the appropriate operating window for each weld setup and related it to its heat conduction characteristics. Welds were sufficiently long to enable determination of the steady-state operating window; this window was found to be much narrower than windows determined by shorter welds. Joint properties were determined at various points within the operating windows.

9:50 AM
Unpredictable Stress Corrosion Crack Growth in Friction Stir Welded 7075 Al: *Christian Fuller*[1]; Murray W. Mahoney[1]; Jesse B. Lumsden[1]; Leanna M. Micona[2]; Mike Hyatt[2]; [1]Rockwell Scientific, 1049 Camino Dos Rios, Thousand Oaks, CA 91360 USA; [2]The Boeing Company, Seattle, WA USA

Stress corrosion (SC) crack growth behavior of friction stir (FS) welded 7075 Al was investigated with constant displacement double cantilever beam specimens. The chevron notch was located at the interface between the FSW nugget and the heat-affected zone. As-FS welded specimens were loaded at one of four locations: advancing side of tool and parallel to the weld direction; retreating side of tool and parallel to the weld direction; advancing side of tool and opposite the weld direction; or retreating side of tool and opposite the weld direction. SC crack growth depended on the loading location. Cracks loaded parallel to the weld direction ran straight providing both crack growth rate and threshold data, while cracks loaded opposite to the weld direction turned 90° from the loading axis. This work illustrates that SC crack growth in as-FS welded 7075 Al can be unpredictable and depends on loading direction.

10:10 AM
Effect of Processing Variables and Tool Design on the Corrosion Properties of FSW AA7050: *Jesse B. Lumsden*[1]; Christian Fuller[1]; Murray W. Mahoney[1]; [1]Rockwell Scientific Co., Matl. Scis., 1049 Camino Dos Rios, Thousand Oaks, CA 91360 USA

Although melting does not occur during friction stir (FS) welding, temperatures are sufficiently high and times at temperature are long enough to cause changes in the microstructure. The altered microstructures in FS welded high strength Al alloys are sensitized making them more susceptible to stress corrosion cracking (SCC), intergranular corrosion, and pitting corrosion than the parent material. Recent investigations indicate that tool design and processing variables can have a significant impact on the SCC susceptibility of FSW AA7050. Pronounced improvements in SCC resistance are obtained by altering

the conventional threaded pen and flat shoulder geometries when the travel speed is optimized. These SCC results will be discussed and related to temperature measurements and an evaluation of the microstructure. This work was sponsored by the Office of Naval Research, Project N00014-02-0212.

10:30 AM Break

10:50 AM Cancelled
Progress in Friction Stir Welding of Thick Section Aluminium Materials

11:10 AM
Microstructure, Fatigue Crack Growth, and Corrosion in Friction Stir Welded Al 5456: *Peter S. Pao*[1]; Richard W. Fonda[1]; Harry N. Jones[1]; Brian J. Connolly[2]; Alison J. Davenport[2]; [1]Naval Research Laboratory, Washington, DC 20375 USA; [2]University of Birmingham, Birmingham UK

The microstructure, mechanical properties, fatigue crack growth and corrosion behavior of friction stir welded Al 5456 were investigated. TEM studies reveal substantial decreases in dislocation density in the HAZ and weld nugget, as compared to the base plate, giving rise to a uniformly lower microhardness across those regions. Longitudinal yield strength also decreases toward the center of the weld. In the nugget region, serrated flow initiates immediately upon yield, while in the base plate such serrated flow does not occur until a critical strain is reached. Fatigue crack growth rates in the HAZ are significantly lower and the fatigue crack growth threshold significantly higher than those in the weld nugget and the base plate. Anodic scans across the weld region, using a microelectrochemical cell, indicate the highest anodic reactivity in the nugget region. These results will be discussed in terms of the observed microstructure in various regions of the weld.

11:30 AM
Friction Stir Welding of Dissimilar Aluminum Alloys: *Robert Cook*[1]; William J. Arbegast[1]; Sean Long Fox[2]; Tito Handby[2]; [1]South Dakota School of Mines and Technology, Advd. Matl. Procg. Ctr., 501 E. St. Joseph St., Rapid City, SD 57701 USA; [2]Oglala Lakota College, PO Box 370, Kyle, SD 57752 USA

Friction stir welding has been shown to be successful in the joining of dissimilar aluminum alloys in longitudinal butt joints. The results of process parameter optimization studies for 0.25 inch thick 2024-T3 to 7075-T73 butt joints alternating on the advancing side and the retreating side are presented. The influence of processing parameters on advancing and retreating side alloy selection on X-, Y-, and Z- axes forces, observed metal flow patterns, and defect formation are presented in terms of the FSW Metalworking Model. Mechanical property, bend test, and intergranular corrosion testing of the dissimilar metal couples are discussed in terms of processing parameters.

11:50 AM
Fatigue of Pre-Corroded 2024-T3 Friction Stir Welds: Experiment and Prediction: *Ulises Alfaro*[1]; Tommaso Ghidini[1]; Claudio Dalle Donne[1]; [1]DLR -German Aerospace Center, Inst. of Matls. Rsch., Linder Hoehe, Koeln, Germany 51147 Germany

Friction Stir Welding has been identified as "key technology" by aerospace industry, due to the high mechanical properties of the joint. However, there is still lack of information about the damage tolerance of corrosion susceptible aluminum alloy FSW-joints (i.e. 2xxx, 7xxx). In this investigation 2024-T3 base metal and FSW-joints were pre-corroded with an alternate immersion technique (ASTM G44) in a 3.5% NaCl aqueous solution for 100, 250 and 1000h. SN fatigue strength of the pre-corroded specimens were carried out in laboratory air using different R-ratios (R=-1, 0.1, 0.5). Maximal pit geometry (width and depth) criteria were used as initial crack in a linear-elastic model to predict the fatigue life of the specimens. Numeric simulations were realized with help of AFGROW and NASGRO software. The obtained prediction results are quite close to the experimental data.

12:10 PM
The Effect of Spot Friction Welding (SFW) Parameters on the Strength and the Microstructure of Aluminum 6111-T4 Lap Joints: *David Mitlin*[1]; Tsung-Yu Pan[2]; Michael L. Santella[3]; Zhili Feng[3]; [1]University of Alberta, Cheml. & Matls. Engrg., Edmonton, Alberta T6G 2G6 Canada; [2]Ford Research and Advanced Engineering, Mfg. & Processes, Rm. 2345-1, M/D 3135, SRL Bldg., Dearborn, MI 48124 USA; [3]Oak Ridge National Laboratory, Metals & Ceram. Div., Oak Ridge, TN 37831-6096 USA

Spot friction welding (SFW) is a new solid-state welding process that utilizes a rotating tool with a probe pin to create spot welds in lap configurations. Unlike the linear friction stir welding (FSW) process, where the tool moves in the transverse direction to form a continuous linear butt joint, in SFW the tool is not translated. Instead, the tool is retracted from the workpiece when the stirring process is finished at a particular spot. We examined the influence of weld parameters such as tool rotation speed, tool hold time and tool downward force on the strength of aluminum 6111-T4 lap-joints. We have also characterized the subsequent microstructures near the weld nugget, the thermo-mechanically effected zone and the heat affected zone using scanning and transmission electron microscopy. Specific issues addressed are the effect of weld parameters on texture evolution, on precipitate/zone reversion and subsequent re-formation, and on the dislocation content of the affected areas.

12:30 PM
Precision Friction Stir Welding of Vacuum Processing Chambers: *Jack Thompson*[1]; [1]General Tool Company, 101 Landy Ln., Cincinnati, OH 45215 USA

Processing chambers of high-vacuum semiconductor fabrication equipment have typically been machined from solid billets of aluminum, machined from aluminum castings, or dip-braze fabricated from pre-machined aluminum plates. Fusion weldments of aluminum plates have typically been avoided because of porosity in the welds, particularly when welds are machined for o-ring grooves. Friction Stir Welding is an attractive new alternative means of chamber fabrication because it combines the best attributes of solid wrought aluminum, including the absolute lack of porosity, with significant reductions in machining and wasted material. General Tool has recently completed a production run of these chambers, and has developed means of holding machining tolerances on the pre-machined internal features of the chamber.

Frontiers in Solidification Science: Morphological Evolution and Mushy Zone Phenomena I

Sponsored by: Materials Processing & Manufacturing Division, MPMD-Computational Materials Science & Engineering-(Jt. ASM-MSCTS), MPMD-Solidification Committee
Program Organizers: Ralph E. Napolitano, Iowa State University, Ames Laboratory, Department of Materials Science and Engineering, Ames, IA 50011 USA; James R. Morris, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6115 USA

Monday AM Room: 2020
February 14, 2005 Location: Moscone West Convention Center

Session Chairs: Alain Karma, Northeastern University, Boston, MA 02115 USA; Peter W. Voorhees, Northwestern University, Evanston, IL 60208 USA

8:30 AM Opening Remarks

8:40 AM Keynote
Conduction-Limited Melting of Mushy Zones: *Martin E. Glicksman*[1]; [1]Rensselaer Polytechnic Institute, Matls. Sci. & Engrg. Dept., 110 8th St., CII-9111110 8th St., Troy, NY 12180-3590 USA

The formation and melting of dendritic mushy zones of pivalic acid were observed under convection-free conditions as part of NASA's United States Microgravity Payload Mission, flown on the space shuttle Columbia in 1997. Video data show that in microgravity dendrites melt without relative motion or settling with respect to the quiescent melt phase. Individual mushy-zone fragments follow a square-root time-dependence as predicted using quasi-static conduction-limited theory. Agreement between theory and experiments is found when the melting of individual crystallites occurs under shape-preserving conditions (constant axial ratio). Interactions among crystallites in the mushy zone, however, inevitably result in thermal shielding and shape changes and, as melting progresses, other complicating effects such as capillarity enter the process. Our recent shape analysis of melting dendritic fragments show that slender crystallites (axial ratios up to 20) exhibit strong capillary effects when their major axis dimensions decrease below 5 mm.

9:25 AM Invited
Adiabatic Remelting of the Mushy-Zone During Rapid Solidification: *Douglas M. Matson*[1]; Robert W. Hyers[2]; [1]Tufts University, Mechl. Engrg., 025 Anderson Hall, 200 Coll. Ave., Medford, MA 02155 USA; [2]University of Massachusetts, Dept. of Mechl. & Industl. Engrg., Engrg. Lab Bldg., 160 Governers Dr., Amherst, MA 01003 USA

Following primary metastable recalescence, the first stage of microstructural evolution involves growth of the stable phase into the mushy-zone. The stable phase growth rate can be predicted using a simple dendrite growth model if the heat balance is modified to include

isothermal melting of the pre-existing solid. This adiabatic remelting model successfully predicts the growth rates for the stable phase as measured experimentally in the Fe-Cr-Ni alloy system. The growth rate of the stable phase depends strongly on composition, but this dependence is countered by a reduction in the heat absorbed through melting of the metastable solid. Due to the small variation in thermophysical properties over a wide range of compositions, the net result of these two competing effects is a constant heat flux which is independent of composition.

10:00 AM Invited
Transition of the Mushy Zone from Continuous Liquid Films to a Coherent Solid: *Michel Rappaz*[1]; Stephane Vernède[1]; [1]EPFL, Inst. of Matls., Computational Matls. Lab., Lausanne CH-1015 Switzerland

While studies of solidification microstructures have focused mainly on the tips of the dendrites, the last stage solidification is equally important from the point of view of defect formation (porosity, hot tearing), mechanical strength build-up and precipitation of phases. In particular, the transition from continuous liquid films to a coherent solid in low concentration alloys is of crucial importance for hot tearing formation, and more generally speaking for liquid feeding ability and coherency development. Based on a fairly recent theoretical model of coalescence which will be recalled briefly, new results obtained for a population of equiaxed grains will be presented. A granular-type model based on a Voronoï tessellation has been used for the description of the gradual disappearance of liquid films and the clustering of equiaxed grains. This percolation-type approach has been used then to calculate the pressure drop in the mushy zone on the assumptions of a Poiseuille flow in between the grains and a Kirchoff model for the connectivity of the liquid films including the Losses associated with solidification shrinkage (i.e, PKL model). Comparison with a standard average pressure drop calculation based on Carman-Kozeny's relationship will be presented.

10:35 AM Break

10:55 AM Invited
Phase-Field Simulations of Coupled Columnar and Equiaxed Dendritic Growth: *Christoph Beckermann*[1]; Arnoldo Badillo[1]; Juan C. Ramirez[1]; [1]University of Iowa, Dept. Mechl. & Industl. Engrg., 2412 SC, Iowa City, IA 52242 USA

Two-dimensional phase-field simulations of coupled columnar and equiaxed dendritic growth are performed for a binary alloy solidifying unidirectional under an imposed temperature gradient. The equiaxed grains nucleate and grow inside the constitutionally undercooled zone ahead of the columnar front. The phase-field model reduces to the sharp-interface equations in a thin-interface limit where kinetic and solute trapping effects are negligible. The computations are performed using an adaptive grid that moves with the solidification front. The competition between the columnar and equiaxed dendrites is investigated as a function of the nucleation undercooling, the equiaxed grain density, and the imposed cooling rate and temperature gradient. The conditions leading to a columnar-to-equiaxed transition are examined in detail and compared to theoretical models. Future needs in simulating grain structure development in solidifying alloys are discussed.

11:30 AM Invited
Cellular Pattern Selection in Directional Solidification: *Rohit Trivedi*[1]; Shan Liu[1]; Blas Echebarria[2]; Alain Karma[2]; [1]Iowa State University, Matls. Sci. & Engrg., 100 Wilhelm Hall, Ames, IA 50014 USA; [2]Northeastern University, Dept. of Physics, 110 Forsyth St., Boston, MA 02115 USA

Although significant advances have been made in the planar and dendritic interface growth, our understanding of cellular pattern formation has remained incomplete. Due to the strong coupling of solute field between the neighboring cells, significant variations in cell shapes and cell spacing are present for different cells in an array that has precluded a proper quantitative description of cellular growth. Through detailed experimental studies and phase-field modeling, we have found that all cells in an array follow a definite scaling law in that all cell shapes collapse (within optical resolution) onto a single shape when they are scaled with the local spacing. This shape interpolates between the two known limits of this problem: the Scheil equation and the 2D Saffman-Taylor (ST) equation which describes the Laplacian limit of directional growth. The former predicts the asymptotic shape of the interface far from the tip while the latter is found here to predict reasonably well the cell tip of experimental and numerical cell shapes. An expression for the cell tip undercooling is obtained from the results of the phase-field model, which is found to be in good agreement with the result based on the ST shape and with the result obtained experimentally in the succinonitrile-salol system. In the limiting case, when an intercellular eutectic is present, the cell shape is shown to follow accurately the solution of the 3D ST problem. Finally, it is found that the phase-field results are strikingly different for 2D shapes and 3D axisymmetric shapes: steady-state cells exist in 2D over a very wide range of spacing, but they only exist in 3D up to a certain maximum spacing only. The existence of this band gap in 3D cell solutions is consistent with previous numerical solutions of the 3D ST problem. Experimental results for 3D cells and phase-field results on 3D non-axisymmetric cells will be presented to give insight into the complex nature of the stability of cellular arrays in 3D.

12:05 PM
Crossover Scaling of Wavelength Selection in Directional Solidification of Binary Alloys: Michael Greenwood[1]; Mikko Haataja[1]; *Nikolas Provatas*[1]; [1]McMaster University, Matls. Sci. & Engrg. & Brockhouse Inst. for Matls. Rsch., 1280 Main St. W., Hamilton, Ontario L8S 4L7 Canada

The selection of microstructure length scales in metal alloys is critical to their mechanical properties. Understanding the kinetics of dendritic pattern selection during solidification is therefore essential to be able to optimize their performance. In this talk we report on simulated cellular and dendritic spacing selection in directional solidification of dilute binary alloys using a phase-field model solved with adaptive-mesh refinement. The spacing of primary branches is examined for a range of pulling velocities, thermal gradients and alloy compositions. It is found to undergo a maximum as a function of pulling velocity, in agreement with experimental observations. Using power spectral analysis we demonstrate that wavelength selection is unambiguously described by a crossover scaling function from the emergence of cellular growth to the onset of dendritic fingers. The construction of the crossover scaling function and length scales is discussed, and our results are validated using previously published experimental data on directional solidification.

Frontiers in Thin Film Growth and Nanostructured Materials: A Symposium in Honor of Prof. Jagdish Narayan: Nanostructures and Nanocomposites I

Sponsored by: Electronic, Magnetic & Photonic Materials Division, EMPMD-Thin Films & Interfaces Committee
Program Organizers: N. (Ravi) M. Ravindra, New Jersey Institute of Technology, Department of Physics, Newark, NJ 07102 USA; Orin Wayne Holland, University of North Texas, Department of Physics, Denton, TX 76203 USA; Sungho Jin, University of California, Department of Materials Science, La Jolla, CA 92093 USA; Stephen J. Pennycook, Oak Ridge National Laboratory, Sold State Division, Oak Ridge, TN 37831 USA; Rajiv K. Singh, University of Texas, Austin, TX 78758-4455 USA

Monday AM — Room: 3020
February 14, 2005 — Location: Moscone West Convention Center

Session Chairs: Sungho Jin, University of California, Matls. Sci., La Jolla, CA 92093 USA; Anthony T. Fiory, New Jersey Institute of Technology, Physics, Newark, NJ 07102 USA

8:30 AM Keynote and Introduction by John C.C. Fan, Chairman and CEO, Kopin Corp. Highlights of J. Narayan's Contribution to Materials Science and Engineering

8:45 AM Invited
Laser Processing of Polymeric and Living Biomaterials: How Can We Leverage Natures Nanotechnology?: *Douglas B. Chrisey*[1]; [1]Naval Research Laboratory, 4555 Overlook Ave., Washington, DC 20375-5345 USA

Today, there are countless applications for thin film coatings made from novel biocompatible materials including medical implants, drug coatings, and bioelectronic interfacing and the implementation of these new materials is expected to improve both device capabilities and performance. Pulsed lasers have unique qualities that can be applied to process biomaterial thin films and they have proven to be an invaluable tool in the research and development. At NRL, we have developed advanced laser-based processing technologies for the deposition of biomaterials including polymers and living biomaterials. We have demonstrated the ability to fabricate novel 3-D tissue constructs using a unique laser forward transfer process that deposits cells using a CAD/CAM process engineered tissue constructs cell-by-cell in order to simulate native structured tissue. But we don't have to re-create the tissue construction with complete fidelity for once the cells communicate, they ride the path evolution has taught. Powered by this break-

through in biomaterial processing, we can now enhance understanding, development, and exploitation of the field of tissue engineering by the ability to group and order specific, defined populations of cells and bioscaffolding with precision. The goal is to demonstrate specific biological function by engineering tissue constructs consisting of well-defined heterogeneous mammalian cell populations.

9:15 AM Invited
Laser Preparation and Characterization of Different Iron-Based Core-Shell Nanostructures: Foreseen Applications: Josef Pola[2]; *Rodica Alexandrescu*[1]; Ion Morjan[1]; Ion Voicu[1]; Florian Dumitrache[1]; Iuliana Soare[1]; Lavinia Albu[1]; Monica Savoiu[1]; [1]National Institute for Lasers, Plasma & Radiation Physics, Lab. of Laser Photochmst., 111 Atomistilor St., PO Box MG 36, Bucharest 76900 Romania; [2]Academy of Sciences of the Czech Republic, Inst. of Cheml. Process Fundamentals, Laser Chmst. Grp., Prague 6 165 02 Czech Republic

The processing of coated magnetic nanoparticles raises great technological interest. Among others, coating provides a matrix for binding of the particles, prevents grain growth and agglomeration, prevents the surface oxidation of the nanoparticles and environmental degradation, would likely enhance the stiffness, toughness, and service life of the composite coating. As such they are potential candidates for applications in data storage, computing, sensing, medicine etc. Among different methods used for Fe encapsulation the laser pyrolysis method is one of the few techniques able to produce nanostructured composites in the nanometer size domain (around 10 nm or even less), with controlled size distribution and chemical composition. This presentation will focus on two examples in which the laser pyrolysis technique is used in a non-conventional geometry of irradiation for the synthesis of i) siloxane polymer-iron/iron oxide shell-core nanostructures (prepared by IR laser-induced and ethylene-photosensitized co-decomposition of iron pentacarbonyl and methoxytrimethylsilane) and ii) iron-carbon core-shell nanoparticles (obtained from ethylene/acetylene/Fe(CO)5 mixtures). The morphology; size distribution chemical content of the nanocomposites are demonstrated by different performant characterization methods.

9:45 AM Invited
Breakthroughs in Optimization of Mechanical Properties of Nanostructured Metals and Alloys: *Carl C. Koch*[1]; *Khaled M. Youssef*[1]; Ronald O. Scattergood[1]; K. Linga Murty[1]; Donald W. Brenner[1]; [1]North Carolina State University, Matls. Sci. & Engrg., 233 Riddick Bldg., 2401 Stinson Dr., Raleigh, NC 27695-7907 USA

The mechanical behavior of nanostructured materials has been a topic of great interest in recent years for the promise of superior properties. While it was predicted that both strength and ductility would be dramatically increased by decreasing grain size to the nanoscale, in general, the strength and hardness were indeed found to be greatly enhanced, but ductility was disappointingly low. Hardness increases of 5 to 10 times that of conventional grain size metals were observed, but ductilities were reduced to very low values, typically less than 2% elongation in tension for metals with grain sizes < 25 nm. Recently, however, some examples of optimized strength and ductility have been reported in nanostructured metals and alloys, in the authors' laboratory and in the literature. This talk will describe these breakthroughs in the mechanical behavior of nanostructured materials and discuss the possible reasons for these superior properties.

10:15 AM Break

10:30 AM
Syntheis and Properties of Nanostructured Magnetic Materials: *D. Kumar*[1]; [1]North Carolina A & T State University, Dept. of Mechl. Engrg., Greensboro, NC 27411 USA

The key to the successful fabrication of nanostructured magnetic materials with improved properties is the development of smart material systems by material-engineering and understanding the fundamentals of materials science. It is in this context that we have developed a novel smart thin film processing method based upon pulsed laser deposition to process nanocrystalline materials with accurate size and interface control with improved magnetic properties. Using this method, single domain nanocrystalline Fe and Ni particles in 5-10 nm size range were embedded in amorphous and crystalline alumina and TIN matrices. By controlling the size distribution in confined layers, it was possible to tune the magnetic properties from superparamagnetic to ferromagnetic in a controlled way. Such growth processing is driven by an underlying instability, such as misfit strain in heteroepitaxial systems. The uniformity in particle size distribution arises from a competition between the thermodynamic instability and kinetic effects. In this talk we will also demonstrate that in multilayer structures, buried dots can influence the nucleation in subsequent layers, leading to self-organization of a more ordered and uniform array. Another interesting accomplishment of our present work that we will like to share is structural characterization of nanostructured magnetic materials using techniques with probe size of atomic dimension so that an unambiguous information are obtained. Understanding the atomic structures and chemistry of nanoparticles and particle-host matrix interfaces is often critical to structure-property relationship in solid state structures of nanoscale dimension. We have employed scanning transmission electron microscopy with atomic number contrast (STEM-Z) and energy loss spectroscopy (EELS) to understand the atomic structure of Ni and Fe nanoparticles and interface between the nanoparticles and the surrounding matrices. Since Z-contrast imaging and EELS could be performed simultaneously, we were able to make direct correlations between structure and chemistry of the Ni and Fe nanoparticles. It was interesting to learn from EELS measurements at individual grains and interface planes that Ni in alumina matrix does not from an ionic bond at the interface indicating the absence of metal-oxygen bond at interface. The absence of metal-oxygen bond, in turn, suggests the absence of any dead layer on Ni nanoparticles even in an oxide matrix. This talk will also highlight some of the research activities pioneered by Prof. J. Narayan in the area of nanomaterials.

11:00 AM
Strengthening Mechanisms in Nanostructured Layered Materials: *Xinghang Zhang*[1]; Amit Misra[2]; Haiyan Wang[2]; Richard G. Hoagland[2]; [1]Texas A&M University, Dept. of Mechl. Engrg., College Sta., TX 77843-3123 USA; [2]Los Alamos National Laboratory, Matls. Sci. & Tech. Div., Los Alamos, NM 87545 USA

Sputter-deposited multilayer composites exhibit very high strength as the bilayer period approaches a few nanometers. Strengthening at layer thickness of greater than tens of nm can be described by dislocation pile-up model, whereas hardening of multilayers at smaller layer thickness, from tens of to a few nm, is not well understood. I will briefly review the strengthening mechanisms in multilayer films that are currently believed to be operative at nanometer length scale. Specific examples on strengthening in Cu/austenitic stainless steel multilayers are given in an attempt to explore the role of interface on strengthening at nanometer length scales. Apart from layer interface induced strengthening, we have recently demonstrated twin interface induced strengthening in single-phase 330 stainless steel films. The high strength is attributed to the resistance to single dislocation transmission across twin interfaces, which are parallel to the surface of substrates and separated a few nm spacing. A model is deve loped that accounts for the formation of nanoscale twins during sputter deposition in terms of the twin boundary or stacking fault energy and deposition rate. Molecular dynamics simulations confirm that at nanometer length scales where plasticity is controlled by the motion of single rather than pile-ups of dislocations, twin boundaries are very strong obstacles to slip. These observations provide a new perspective to producing ultra-high strength metals by utilizing growth twins with nanometer-scale spacing.

11:30 AM
Growth Textures of Nanocrystalline Fe-Ni Alloy Foils: *Yong Bum Park*[1]; [1]Sunchon National University, Matls. Sci. & Metallurgl. Engrg., Maegog-dong 315, Sunchon, Chonnam 540-742 Korea

The texture evolution due to grain growth that takes place during annealing was investigated in nanocrystalline Fe-Ni alloys fabricated by using a continuous electroforming method. In the current materials, grain growth occurred in annealing at much lower temperatures than in conventional coarse-grained counterparts. With regard to the macrotextures, the as-deposited textures were of fibre-type characterized by strong {100}and weak {111}components, and the occurrence of grain growth resulted in the strong development of the {111}fibre texture with the minor {100}components. It was clarified using orientation imaging microscopy that abnormal growth of the {111} grains in the early stages of grain growth plays an important role on the texture evolution. The origin of the abnormal grain growth has been discussed in terms of the orientation dependence of energy density.

12:00 PM
Directed Assembly of Metal Nanostructures by Laser-Induced Rapid Spatio-Temporal Surface Modulations: *Chi Zhang*[1]; Wei Zhang[1]; Adam Bauer[1]; Ramki Kalyanaraman[2]; [1]Washington University, Dept. of Physics, St. Louis, MO 63132 USA; [2]Washington University, Ctr. for Matls. Innovation & Dept. of Physics, St. Louis, MO 63130 USA

Thin film nucleation and growth is a self-assembly process where the initial stages naturally consist of nanometer sized clusters. On defect-free isotropic surfaces, these nanoclusters are a result of random walk surface diffusion and binding. The coupled time and length scale in nucleation, as determined by nucleation rate and saturated

cluster density, are determined primarily by growth rate and substrate temperatures. Therefore, appropriate surface temperature modulations could induce morphology changes. In recent work, we presented novel studies showing that the application of a laser-induced repeated and rapid spatio-temporal surface perturbation in-situ with film deposition dynamically directs the assembly of periodic structures. Evidence shows that the assembly is a result of an anisotropic diffusion flux, reevaporation and suppressed nucleation. The experiment consists of physical vapor deposition simultaneous with pulsed laser interference irradiation of a Si(100) surface. Deposition of metal films like Co and Ag or metal oxides like TiOx result in periodic arrays of dot or line-like features whose periodicity and spacing resemble the interference patterns. The size scale of the resulting dot or line-like features can be varied from the nanometer to micron scale by deposition parameters. The rapid spatio-temporal modulation comes from the short fringe spacing (200 to 2000 nm) and short laser pulse width (9 ns). In this work, we present fundamental experimental studies of the influence of these rapid surface modulations that lead to directed assembly of nanostructures. This experimental approach is a simple way to assembly large-area arrays in a single-step parallel process that is likely to lead to a cost effective manufacturing process.

12:15 PM
Self-Assembled Magnetic Nanostructures: Epitaxial Ni on TiN (001) Surface: *Honghui Zhou*[1]; Jagdish Narayan[1]; [1]North Carolina State University, Matls. Sci. & Tech., 2153 Burlington Lab, CB 7916, Raleigh, NC 27695 USA

Self-assembled nickel magnetic nanostructures were grown on epitaxial titanium nitride (001) surface by pulsed laser deposition (PLD) technique. These nanostructures were characterized by conventional and high-resolution transmission electron microscopy (TEM and HRTEM), scanning transmission electron microscopy (STEM) Z-contrast imaging, and X-ray diffraction (XRD) techniques. The results have shown that the growth of nickel on epitaxial titanium nitride (001) surface follows Volmer-Weber growth mode (3D island growth). The predominant orientation of nickel islands observed is Ni (100) // TiN (100), the so-called "cube-on-cube" orientation relation. The islands are faceted with a truncated pyramidal shape and bounded by (111) planes at sides and (100) plane at the top. The two principal axes of the rectangular island bases are close to two orthogonal <011> directions. The island size analysis showed a narrow size distribution, similar to that found in the systems with coherent self-assembled semiconductor islands grown via Stranski-Krastanov mode (2D followed by 3D growth). The islands were not completely randomly distributed; some islands chains were formed along the directions close to <011>. The interaction between neighboring islands through the island-induced strain field is believed to be responsible, to a large degree, for the island size uniformity and the lateral ordering.

Functional Thin Films for Sensors: The Physics and Applications of Functional Thin Films in Sensors

Sponsored by: Electronic, Magnetic & Photonic Materials Division, EMPMD-Thin Films & Interfaces Committee
Program Organizers: Anis Zribi, General Electric Global Research Center, Niskayuna, NY 12309 USA; Jeffrey Fortin, GE Global Research, Niskayuna, NY 12309 USA; Seung H. Kang, Agere Systems, Device and Module R&D, Allentown, PA 18109 USA; Choong-Un Kim, University of Texas, Materials Science and Engineering, Arlington, TX 76019 USA; N. (Ravi) M. Ravindra, New Jersey Institute of Technology, Department of Physics, Newark, NJ 07102 USA; Gerald Schultz, GE Infrastructure, Sensing, Wilmington, MA 01887-4498 USA

Monday AM Room: 3022
February 14, 2005 Location: Moscone West Convention Center

Session Chairs: Anis Zribi, GE Global Research, Micro & Nano Struct., Niskayuna, NY 12309 USA; Jeffrey Fortin, GE Global Research, Micro & Nano Struct., Niskayuna, NY 12309 USA; C. U. Kim, University of Texas, Arlington, TX USA

8:30 AM Opening Comments: Chairperson

8:35 AM Invited
Micromachined Scanning Thermal Probes and Probe Arrays for High Speed and High Resolution Diagnostics of Thin Films: *Yogesh B. Gianchandani*[1]; [1]University of Michigan, Ann Arbor, MI 48109 USA

Scanning-probe microscopy is emerging as a technique of increasing importance in high-resolution diagnostics of thin films. Thermal microscopy, in particular, offers a number of uses beyond the obvious ability to map temperature variations, including, for example, the measurement of Tg on sub-micron features, non-destructive mapping of sub-surface defects in thin films, and non-lithographic thermal patterning of materials. This presentation will review the development and application of micromachined thermal probes and multi-probe arrays that use polyimide as the structural material and thin-film metal for the probe tips and temperature sensors. Both thermistor and thermocouple probes have been developed. The high mechanical compliance afforded by the use of polyimide as a structural material facilitates their use without mechanical feedback, giving high-throughput parallelism a real chance.

9:00 AM Invited
Thin Film Capacitive Micromachined Ultrasonic Transducers: *B. T. Khuri-Yakub*[1]; [1]Stanford University, E. L. Ginzton Lab., Rm. 11, Stanford, CA 94305-4088 USA

Capacitive Micromachined Ultrasonic Transducers (CMUTs), using thin film membranes, have been developed for generating and detecting ultrasound.. Silicon micromachining allows the manufacture of capacitors with thin membranes, very thin gaps, and with electric fields of the order of 109 V/m that enable their competitive performance. It is possible to make CMUTs with over 100% fractional bandwidth, with an electromechanical coupling coefficient close to unity, and to make single element, one-dimensional (1D), and two-dimensional (2D) arrays of thousands of elements, as well as annular arrays. CMUTs have been operated in the frequency range of 100 kHz to 50 MHz, and with a dynamic range of 150 dB/V/Hz. This paper will first review the operation and technology for making CMUTs. The performance and technology will be compared and contrasted to the technology for making piezoelectric transducers and arrays. Finally, examples of 2D and 3D imaging will be presented to confirm the performance of these transducers.

9:25 AM
Nano-Tunable Infrared Thin Film Filters and Emitters for Sensing of Trace Gases: *Lawrence Domash*[1]; Brian Kinkade[1]; [1]Aegis Semiconductor Inc., R&D, 78A Olympia Ave., Woburn, MA 01801 USA

The mid IR contains spectral signatures of atmospheric trace gases including carbon dioxide, carbon monoxide, sulphur dioxide, hydrogen cyanide, water vapor, nitric oxide or methane, whose sensing and measurement are important for pollution control, HVAC, and home and automotive safety. Optical spectroscopic detection is known to be the most sensitive and precise of any detection technique but has been considered too expensive for consumer applications. We describe a new family of miniature nano-tunable narrowband infrared filters based on the thermo-optic properties of thin film semiconductors. Originally developed for fiber optic telecommunications networks at 1.5 µm, the technology has now been extended to the 3-5 µm range, leading to very compact tunable filters with passbands on the order of 0.5% of center wavelength and tuning ranges up to 4% of center wavelength. We describe a prototype carbon monoxide sensor testbed based on a 4550-4650 nm tunable filter and show it is capable of detecting 10 ppm of CO. This level of low-noise detection results from the ability of nano-tunable optical elements to enable the application of advanced signal processing methods. Second, we show how nano-tunable thin film filters can be integrated with miniature blackbody sources in TO-5 cans to create a new family of ultra low cost integrated tunable IR emitters (named Firefly(tm)).

9:50 AM
Temperature Dependent Infrared Properties of InP, AlN and Al_2O_3: *N. M. Ravindra*[1]; Anthony T. Fiory[1]; Stephen Rubin[1]; Sudhakar Shet[1]; Vishal R. Mehta[1]; Sreeya Srivatsa[1]; [1]New Jersey Institute of Technology, Newark, NJ 07102 USA

A spectral emissometer operating in the wavelength range of 1 to 20 microns and temperature range of 25 to 1000ºC has been deployed to measure the optical properties of InP, AlN and Al2O3. The measured reflectance, transmittance and emittance of these materials have been compared with available optical properties in the literature. Phenomenological approaches are subsequently employed to deconvolute the measured optical properties to yield wavelength and temperature dependent fundamental optical constants.

10:15 AM Break

10:35 AM
Interaction of Metal Oxide Sensitive Layer With Ambient Atmosphere at Varying Sensor Working Temperature: *Tadeusz*

Pisarkiewicz[1]; Wojciech Maziarz[1]; Krzysztof Hajduk[1]; [1]AGH University of Science and Technology, Dept. of Elect., Al. Mickiewicza 30, Krakow 30-059 Poland

Semiconductor resistive gas sensors are known from their poor selectivity and resistance drift. The exact knowledge of the mechanism of gas/ oxide semiconductor surface interaction enables the optimal selection of gas sensor working regime. The authors have performed the analysis of semiconductor surface reactions with oxygen atmosphere and the influence of chemisorbed oxygen concentration on sample conductance was calculated. Further the influence of reduction and other oxidizing gases on the sensor surface has been envisaged. The model calculations were performed for different temperature operation modes, i.e. sinusoidal, pulse and triangle and the resuls compared with experimental observations. The adequate choice of model parameters results in output signals with good agreement with experimental sensitivity characteristics for thin SnO2 sensitive layers deposited onto multilayer ceramic or micromachined silicon substrates.

11:00 AM

Novel Single Crystal Model for Semiconducting Oxides Thin Film Gas Sensors: *Satyajit Shukla*[1]; Sudipta Seal[1]; [1]University of Central Florida, AMPAC & MMAE Dept., Engrg. 381, 4000 Central Florida Blvd., Orlando, FL 32816 USA

It has been recognized that the gas sensitivity, as well as the response and the recovery time of a semiconducting oxides thin film sensor, depend on number of parameters, such as nanocrystallite size, film thickness, nature and amount of dopants, surface catalyst and foreign oxides, amount of film porosity, and operating temperature. Interestingly, a theoretical model, which would give the effect all these variables on the gas sensitivity has not been yet reported in the literature. In view of this, we propose here a new constitutive equation for the gas sensitivity of nanocrystalline semiconducting oxide sensors based on a single crystal model. The present theoretical model describes the relationship between the gas sensitivity, nanocrystallite size, film thickness, Debye length, operating temperature, surface coverage, and lattice oxygen-ion-vacancy concentration. The validity of the proposed theoretical model is justified by comparing the model predictions with the reported experimental results.

11:25 AM Invited

Water Thin Film Nano-Scale Transistor for Chemical Sensing: *M. Willander*[1]; Z. Chiragwandi[1]; O. Nur[1]; [1]Chalmers University of Technology and University of Göteborg, Physl. Elect. & Photonics, Physics & Engrg. Physics, SE-412 96 Göteborg Sweden

In this invited paper, we present a Si compatible nano-scale water based transistor. The device composed of two nano-electrodes and a third electrode for controlling and manipulating the pH of water The water film thickness can be as thin as 1 µm. By controlling the base electrode, the pH of the water can be manipulated, and a transistor action is observed between two nano-electrodes (emitter and collector). Different device configurations are investigated in view of the effect of the nano-electrodes spacing (emitter-collector spacing) as well as the position and design of the pH electrode (base). The DC characteristics will briefly be discussed in view of the water ions decomposition and it's dependence on the transistor configuration. Time dependant measurement will be presented and discussed both theoretically and correlated to experimental results. Dynamics of ions in water and it's relation to pH will also be discussed. Conversion of chemical reaction(s) to an electrical signals in a well controlled way will be shown and discussed. Finally, and due to the presence of water in almost most chemical reactions as well as biological activities, the importance of the newly presented device will be highlighted.

11:50 AM

Room Temperature Hydrogen Gas Sensitivity of Nanocrystalline Doped-Tin Oxide Sensor Under Ultraviolet Light: *Satyajit Shukla*[1]; Lawrence Ludwig[2]; Rajnikant Agrawal[1]; Julian Duarte[1]; Hyoung Cho[1]; Sudipta Seal[1]; [1]University of Central Florida, Advd. Matls. Procg. & Analy. Ctr. (AMPAC) & Mechl. Matls. Aeros. Engrg. (MMAE) Dept., Engrg. 381, 4000 Central Florida Blvd., Orlando, FL 32816 USA; [2]Kennedy Space Center, KSC-NASA, FL 32899 USA

Nanocrystalline indium oxide doped-tin oxide thin film is sol-gel dip-coated on microelectromechanical-systems (MEMS) device. Effect of ultraviolet (UV) radiation on room temperature hydrogen sensitivity of the present sensor is systematically studied. Freshly prepared sensor exhibits higher hydrogen sensitivity under UV-exposure than that without UV-exposure, in agreement with earlier reports. However, sensor behavior is observed to reverse after initial UV-exposure, which is attributed to the burning of carbonaceous impurities from the sensor-surface. It is observed that subsequent exposure to UV-radiation results in deterioration of hydrogen sensitivity of the present sensor. Very high hydrogen sensitivity as high as 110000 is observed, for 900 ppm hydrogen in dark condition. However, in the presence of UV-radiation, hydrogen sensitivity is reduced to 200. The drastic reduction in hydrogen sensitivity under UV-exposure is explained on the basis of the constitutive equation for the gas sensitivity of nanocrystalline semiconducting oxides thin film sensor proposed by present authors.

General Abstract Session: Electronic Materials

Sponsored by: TMS

Program Organizers: Thomas R. Bieler, Michigan State University, Department of Chemical Engineering and Materials Science, East Lansing, MI 48824-1226 USA; John J. Chen, University of Auckland, Department of Chemical & Materials Engineering, Auckland 00160 New Zealand; James C. Earthman, University of California, Department of Chemical and Materials Science, Irvine, CA 92697-2575 USA

Monday AM Room: 2011
February 14, 2005 Location: Moscone West Convention Center

Session Chair: James C. Earthman, University of California, Dept. of Cheml. Engrg. & Matls. Sci., Irvine, CA 92697-2575 USA

8:30 AM

Wafer Integration of GaN/GaN and Al0.25Ga0.75N/GaN Through Wafer-Bonding Technology: *Frank F. Shi*[1]; [1]University of Illinois, Micro & Nanotech. Lab., 208 N. Wright St., Dept. of Electl. Engrg., Urbana, IL 61801 USA

Group III-nitride-based wide-bandgap semiconductors, such as GaN, AlN, and their ternary alloy AlxGa1-xN have emerged as the leading materials for a variety of key applications in advanced integrated optoelectronics. One of the major challenges in group-III nitride semiconductors is the heterointegration of free-standing GaN-based devices with dissimilar substrates. Wafer bonding, as one of the encouraging material and device integrating techniques, has become an enable approach to fabricate hybrid-integrated heterostructures with multiple bandgaps. In this study, the wafer integration of GaN/GaN and Al0.25Ga0.75N/GaN semiconductors through direct bonding technology was reported. The surface morphologies of pre-bonding and debonded wafers were characterized by Atomic Force Microscope (AFM). Scanning Electron Microscope (SEM) and Transmission Electron Microscope (TEM) were employed to study the epitaxial structures and the bonded interface micromorphologies. The interface adhesion was estimated based upon the measured interface fracture energy Go from double cantilever beam (DCB) technique, and the interface fracture energies of several different wafer-bonded III-V semiconductors were also compared. By comparing the atomic chemical bond energy Eo with the interface fracture energy Go, the bondability of a few major III-V semiconductors were analyzed. The potential effects from surface and interface microstructures on the wafer bondability and interface adhesion were discussed. It has been found that the relatively strong wafer bonding of group III-nitride was typically realized at 1000°C. From AFM scanning, it was found that the debonded wafer surfaces generally have much higher surface roughness than the pre-bonding wafers. The wafer bondability and bonding process conditions depend heavily on the surface topography of the pre-bonding wafer surfaces. Lower wafer surface roughness is expected to provide better bondability and demand less stringent bonding conditions. The Ga droplets due to GaN dissociation and Ga extraction were observed on the debonded GaN wafer surface. Interface fracture energies Go of bonded group III- nitrides are higher than those of other bonded III-V semiconductor wafers due to the nature of their stronger chemical bonds and the closer-packed plane at (0001) direction. It was also observed that the measured interface fracture energies of water-bonded semiconductors are generally about 40% of the overall atomic chemical bond energy on the same unit are a, which mainly resulted from the large density of dangling bonds and other imperfections at the wafer-bonded interfaces. High resolution SEM and TEM images on the wafer-bonded interfaces of GaN/GaN and Al0.25Ga0.75N/GaN show an uniformly distrusted amorphous thin layer and the previously observed nanoinclusions in other wafer-bonded semiconductors were not found due to the fact that it was thermally difficult to rearrange group III-nitride atoms and to recrystallize the bonded interface between the two group III-nitride wafers.

9:00 AM
Hot-Wall CVD Epi-Growth of 4H-SiC Using PVT Buffer Layer: *Ying Gao*[1]; [1]Bandgap Technologies, Inc, 1428 Taylor St., Columbia, SC 29201 USA

Physical vapor transport (PVT) has been successfully used for SiC bulk growth. Recently, this method has been proposed for the growth of thick epilayer, however, due to the extremely high temperature required for implementing this process, it is very hard to control the doping level during epi-growth. Therefore, chemical vapor deposition (CVD) is still the main approach to achieve high quality epitaxial film in SiC for device application. But good quality CVD film requires very high quality substrate and is very sensitive to surface preparation. The defects existing in the substrate, such as micro-pipes, dislocations, scratch marks will propagate to the epilayer during growth. Moreover, a great number of new defects will be generated in the initial epi-growth due to the existence of the huge thermal stress formed by different growing temperatures for substrate (more than 2300°C) and epilayer (less then 1700°C). In this work, we attempt to make use of PVT to grow a thin buffer layer with high n-type doping, and then grow regular epilayer by CVD on top of it. The PVT buffer layer was grown at 2050°C in the ambient of Ar, which will significantly reduce the thermal stress from substrate and close most of the micro-pipes. Atomic force microscopy (AFM) images showed a bunch of scratch marks appearing on the original commercial wafer surface. After PVT buffer growth, the surface became perfect with no scratch marks owing to the initial etching process of PVT growth and a true micro-pipe free surface was obtained. The RMS roughness was reduced from more than 2 nm to 0.6 nm. In the second step, homoepitaxial growth was carried out in the home-built vertical hot-wall CVD system. SiH_4-C_3H_8-H_2 system was used in CVD growth. The chamber pressure was maintained at 300 Torr. A 10 μm thick epilayer was grown at a growth rate of 15 μm/hr. The epilayer was examined by high resolution optical microscope (HROM), AFM and scanning electron microscopy (SEM). Excellent surface morphology was obtained without features. Furthermore, with the aid of KOH etching and back-reflection X-ray topography, the substrate, the PVT buffer layer and the CVD epilayer will be investigated to determine the variation in defect density, particularly threading and screw dislocations. Further improvement of the epitaxial layer quality will be discussed and suggested.

9:30 AM
Effects of Holmium Oxides on Electrical Properties of BaTiO3 Sputtered Thin Films: *Z. H. Wu*[1]; J. P. Chu[1]; S. F. Wang[2]; T. N. Lin[1]; C. H. Lin[1]; [1]National Taiwan Ocean University, Inst. of Matls. Engrg., 2, Pei-Ning Rd., Keelung 20224 China; [2]National Taipei University of Technology, Dept. of Matls. & Minerals Resources Engrg., Taipei 20224 China

The holmium-doped $BaTiO_3$ thin films deposited on Pt/Ti/SiO_2/Si substrate by r.f magnetron sputtering method were investigated. The effects of post- annealing temperature and dopant concentration were studied. The compositions of thin films measured consist of BT2 (Ba/Ti=0.8543), BT (Ba/Ti=0.9681), BT-0.05Ho, BT-1.1Ho, BT-1.8Ho and BT-2.9Ho where Ho-content was in at%. The dielectric constant of all compositions thin films increased with increasing annealing temperature, presumably due to better crystallinity and large grain sizes. The BT2 film with 200nm thickness annealed at 700°C showed the high dielectric constant of ~287 measured at 100 KHz. In addition, a significant role of the Ho on reduction of leakage current density is observed for the 700°C annealed samples. The BT-2.9Ho film showed the low leakage current density of 1.27×10^{-8} A/cm^2 at an electric field of 100KV/cm.

10:00 AM Break

10:20 AM
Mechanosynthesis Technique to Improve Superconductor Properties of MgB2: Mechanical Alloying-Ball Milling: *Ely X. Colon*[1]; [1]University of Wisconsin and University of Puerto Rico, Applied Superconductivity Ctr., Matl. Sci. & Engrg., PO Box 779, Sabana Seca, P.R. 00952 USA

The present article explains the process used in the development of the mechanosynthesis of superconductor, MgB2 and MgB2 + MB2 using diborides such as ZrB2, AlB2 and TiB2, in order to improve its superconducting properties. These milling devices include the vibrational mills. X-ray diffraction (XRD) and Superconducting Quantum Interface Device measurements, (SQUID) were used in order to identify the phases presented and the characterization of the final product of the samples after conducting mechanical alloying process. The SQUID measurements showed a decrease of the Tc in samples of 10at% TiB2 with 20K to 5K transition. 10at% AlB2 shows a wide transition and lower Tc in comparison with pure MgB2 bulk with a transition Tc from 15K to 5K. The XRD patterns show amorphization behavior for all of the compounds and many impurities and secondary phases that could be the cause for the decrement of Tc.

10:50 AM
True Image Light Amplifier: *Phillip Kornreich*[1]; *Akshob V. Bangle*[1]; [1]Syracuse University, EECS, 121 Link Hall of Engrg., Syracuse, NY 13244 USA

A feeble light with appropriate amplification improves visibility in dark places. This has led to considerable research and development of Night Vision Techniques. Here at Syracuse University, it has been successfully demonstrated that the Semiconductor Cylindrical Fiber Light Amplifiers (SCFLA) provides net gain for optical communication wavelength, which are in the infrared region. For light amplification in the visible spectrum, we have selected a semiconductor compound that would amplify light in this region. We found that the semiconductor Cadmium Germanium Phosphide ($CdGeP_2$) can be used for light amplification since it covers almost the whole visible spectral band from a wavelength of 414nm to about 700nm. We have calculated the light amplification for various pump light induced charge carrier densities. An UV pump laser is used in this application. A graph of the gain produced to the wavelength is shown in the figure. As seen, when the pump induced charge carrier surface density in the semiconductor film of 1.6 X 10^{17} per m2, the gain region covers almost the whole visible spectrum. This semiconductor fiber can amplify light over the whole visible spectrum using only one pixel per image point unlike the usually display devices that uses three different colors to present as an image to a human eye, there by requiring three pixels for each image point. Thus one can build light amplifying plates that are about 4 to 10 mm thick and have sufficient gain.

11:20 AM
A Cellular Automata Model for Dendritic Crystal Growth: *Liang Yu*[1]; Yuanchi Dong[1]; Liaosha Li[1]; [1]Anhui University of Technology, Anhui Provincial Key Lab. of Metallurgl. Engrg. & Resources Recycling, Hudong Rd., Ma anshan, Anhui 243002 China

A cellular automata model was proposed as a simple simulation model for crystal growth patterns in a diffusion field. Parabola-like and dendritic patterns were obtained in two-dimensional cellular automata. The crystal grain growth and its pattern were controlled by parameters of the diffusion field as well as the surface tension effect introduced through parameter in the surface process. As a simple model, the simulation could be easily performed and a variety of growth patterns were possible to be generated by changing the parameters in the model.

11:50 AM
A Comparative Study of Ferroelectric Lanthanide Doped Bismuth Titanate Films Prepared by Sol-Gel and Pulsed-Laser-Ablation: *Ashish Garg*[1]; X. Hu[1]; Z. H. Barber[1]; [1]Indian Institute of Technology, Dept. of Matls. & Metallurgl. Engrg., Kanpur 208016 India

Thin films of ferroelectric Bi-layered Aurvillius perovskite oxides have been an active area of investigation due to their potential applications in non-volatile ferroelectric random access memories (FRAM) and ferroelectric field effect transistor (FET) devices. Among various materials, SrBi2Ti2O9 (SBT) and La-doped bismuth titanate (BLT) have been intensively investigated due to their excellent fatigue resistance on Pt electrodes. In this paper, we present the results of lanthanide–doped (Sm and Nd-doped) bismuth titanate ferroelectric (BLnT) thin films deposited on platinized Si substrates. To study the influence of type process of the film properties, the films were grown by pulsed laser deposition (PLD) and chemical solution deposition (CSD) and structural and ferroelectric properties of the films were evaluated in detail. The structural characterization was done using X-ray diffraction (XRD), Raman spectroscopy and atomic force microscopy (AFM). Detailed ferroelectric measurements were performed to study hysteresis behavior (P-E loops), dielectric constant, leakage behavior (J-V plots), and polarization fatigue. The films deposited by both processes were polycrystalline but the film morphology was dependent on the type of process. Pulsed-laser-ablated Sm-doped Bi4Ti3O12 films on Pt/Si substrates show a remanent polarization (2Pr) as high as ~45 C/cm2. In case of chemical-solution-derived Nd- and Sm-doped Bi4Ti3O12 films grown on Pt/Si substrates, the crystallinity and ferroelectric properties were strongly dependent upon the annealing temperature. All films demonstrate fatigue-free behavior up to 109 read/write switching cycles. Conduction mechanism of the films is found to exhibit a dependence on the type of deposition process.

General Abstract Session: Temperature Treatments and Casting

Sponsored by: TMS
Program Organizers: Thomas R. Bieler, Michigan State University, Department of Chemical Engineering and Materials Science, East Lansing, MI 48824-1226 USA; John J. Chen, University of Auckland, Department of Chemical & Materials Engineering, Auckland 00160 New Zealand; James C. Earthman, University of California, Department of Chemical and Materials Science, Irvine, CA 92697-2575 USA

Monday AM Room: 2012
February 14, 2005 Location: Moscone West Convention Center

Session Chair: Alan W. Cramb, Carnegie Mellon University, Pittsburgh, PA 15213 USA

8:30 AM
Investigation of Recrystallisation Resistance in Al-Hf-(Sc)-(Zr) Alloys: *Haakon Hallem*[1]; [1]NTNU, Dept. of Matls. Tech., Alfred Getzv 2b, Trondheim 7491 Norway

Highly stable microstructures are required to cope with the demand for extruded aluminium alloys tolerant of exposures to temperatures of up to 600°C. In order to achieve this Hf, Sc and Zr were added to Al alloys in different concentrations and combinations. These elements form dispersoids of the type Al3X (X=Hf,Sc,Zr) upon annealing. Cold rolling was applied to the alloys in order to investigate the recrystallisation resistance after deformation. The Al-Sc-Zr alloy has been found to stay unrecrystallised with a heat treatment of 1 hr at 600°C even after 80% reduction. One of the Al-Hf-Sc-Zr alloys did also resist recrystallisation, except for a thin surface layer. Despite the recrystallisation resistance the heat treatments applied cause a considerable loss in strength of all the alloys. But still the unrecrystallised alloys have a higher hardness.

8:55 AM
The Effect of Tempering on Low Cycle Fatigue Behavior of Polycrystalline Al2024: *Aezeden Omar Mohamed*[1]; [1]University of Manitoba, Mechl. & Mfg. Engrg., Mechl. Engrg. Dept., Rm. 356, Winnipeg, Manitoba R3T 2N2 Canada

A low cycle fatigue study on Al2024 polycrystalline alloy was conducted under symmetric tension-compression at room temperature, using a servo-hydraulic testing machine, to investigate the effect of tempering on cyclic deformation. The tests were conducted at constant frequency for O-temper condition and a constant strain rate for T6-temper condition. The fatigue response of the alloy was evaluated macroscopically in terms of cyclic stress strain response and microscopically in terms of appearance of cyclic slip bands. It was found that the cyclic stress strain response of O-tempered alloy exhibited an increase in saturation stress with plastic strain whereas the cyclic stress strain response of T6- tempered alloy exhibited a definite plateau region where the saturation stress remained constant with plastic strain. The T6-temper alloy showed the presence of persistent slip bands (PSBs), which were extending across the grain at 45° orientations from the grain boundary. No (PSBs) were observed in the microstructure of the O-temper alloy; however, precipitate free zone (PFZ) was observed adjacent to the grain boundaries. Needle-like precipitates were also observed within the grains with two different orientations and the angle between them was 65?a in the O-tempered alloy.

9:20 AM
A Differential Scanning Calorimetry Study on Crystallization of Sputtered Ba1-x Sr x TiO3 Thin Films: *Tai Nan Lin*[1]; Jinn P. Chu[1]; Sea-Fue Wang[2]; [1]National Taiwan Ocean University, Inst. of Matls. Engrg., 2 Pei Ning Rd., Keelung 202 Taiwan; [2]National Taipei University of Technology, Dept. of Matls. & Mineral Resources Engrg., Taipei 202 Taiwan

Crystallization behavior of sputtered BST, $(Ba_{0.3}Sr_{0.7})TiO_3$, thin films has been characterized by means of differential scanning calorimetry(DSC) and transmission electron microscopy(TEM). The crystallization of as-deposited amorphous structure to the equilibrium crystalline structure is confirmed as an irreversible, exothermic, first order transition. DSC result confirming the metastable nature of sputtered films is in agreement with that of a conventional, ex-situ X ray diffraction result. At a heating rate of 20°C/min, the crystallization peak temperature of BST film is found to be 697.9°C and to increase with increasing heating rate. Activation energy for crystallization is determined, by Kissinger's method, to be 447.7 kJ/mol. TEM results reveal the presence of amorphous and crystalline phases at temperatures below 750°C, indicating that the substrate temperature below 750°C is not sufficiently high for the full crystallization of the film. Diel ectric constant value increases with increasing substrate temperature, reaching the highest value of ~160 at 750°C.

9:45 AM
Effect Appreciation of Jominy End Quench on the Microstructure and Mechanical Properties of A356 Cast Aluminum Alloys: *Qingcai Liu*[1]; Yungui Du[1]; Xin Huang[1]; [1]Chongqing University, 174 Shapinba St., Chongqing 400044 China

The review to date examines the use of the Jominy End Quench specimen and its application to the examination of the effects of quench rate and subsequent processing on A356 aluminum alloys. Heat treatment for aluminum alloys broadly covers the following: homogenization to eliminate coring developed during solidification; annealing for recovery, recrystallization and grain size control; solutionizing of precipitation strengthening solutes in solid solution; quenching to supersaturate the solid solution for subsequent aging; and aging to precipitate the strengthening phases. The review collected and compiled the current knowledge related to the relationship between the heat treatment process and the microstructure and mechanical properties of A356 aluminum alloys. It was extended to the alloying elements and heat treatment effects on precipitate and microstructure. The experimental technique of the Jominy End Quench was concerned in this work.

10:10 AM Break

10:30 AM
Substitution of Malleable Cast Iron with Ferritic Ductile Cast Iron at Low Temperatures: *Mehran Tadayonsaidi*[1]; Nima Baghersaiee[2]; Naser Varahram[3]; [1]AZAD University, PO Box 31535-3453, Karaj Iran; [2]Engineering Research Institute, Control Dept., Ministry of Jihad Agriculture, Tehran Iran; [3]Sharif University of Technology, Dept. Met. Sci. & Engrg., Tehran Iran

In the past 40 years the use of ductile cast iron has grown rapidly, mainly through conversions from gray and malleable iron casting. In many cases malleable cast iron replaced with ductile iron but it has a higher mechanical property such as elongation and toughness at low temperature. In this study the properties of ferritic ductile cast iron with different percent of silicon and the effect of heat treatment annealing cycles and microstructure on the mechanical properties, as compared to malleable ductile iron were investigated. The results show that Ferritic ductile iron has higher mechanical properties such as yield stress and hardness, which is rised by increasing the amount of silicon contents, also when designing for low temperature application the amount of silicon content should be less than 2% due to the similar impact strength to malleable cast iron at low temperature. Mechanical tests and SEM and optical microscopic investigate the accuracy of these results. The result of this research was so benefit for different industry applications mainly in railway parts which cause to lower costs with the same property comparing to another structure.

10:55 AM
The Effect of Mold Flux on Radiative Heat Transfer: *Wanlin Wang*[1]; Alan W. Cramb[1]; [1]Carnegie Mellon University, 5000 Forbes, Pittsburgh, PA 15213 USA

As an important factor in the moderation of heat transfer in continuous casting mold, the mold flux has been researched widely for varied purposes. However, the study of effect of mold flux on radiative heat transfer has not been conducted much. Through using an infrared radiation emitter, which is developed at Carnegie Mellon University to allow about 1 MW/m2 heat flux to produce, the radiative heat flux is applied to copper mold to simulate the heat transfer phenomena in continuous casting. The effect of adding a thin slag disc on top of copper mold on radiative heat transfer has been analyzed. It has been found that the mold flux plays a very different role by enhancing radiative heat transfer instead of retarding conductive heat transfer. The specific effect of crystalline and glassy parts of the mold flux on radiative heat transfer, and the influence of their properties on heat transfer rate will be discussed in this paper.

11:20 AM
Castability and Microstructure Characterization of Reduced and Lead Free Brasses for Sanitary Applications: *C. Vilarinho*[1]; D. Soares[1]; J. J. Barbosa[1]; F. Castro[1]; [1]University of Minho, Mechl. Engrg., Campus de Azurem, Guimarães 4800 Portugal

As a result of environmental concerns, brass products, namely those which are in direct contact with drinking water, must be manufactured from reduced or lead free alloys. For that purpose a set of brasses, that could substitute the traditional ones, has been developed and cast and

its chemical composition determined by XRF spectrometry. Castability and solidification shrinkage of the alloys were studied using appropriate devices and melting and transformation temperatures were determined by Differential Scanning Calorimetry (DSC). Each alloy was observed by Scanning Electron Microscopy (SEM) to identify the phases present and its chemical analysis was determined by Electron Probe Microanalysis (EPMA). A comparison between the results concerning the developed alloys and the traditional leaded brasses is established.

Globalization of Materials R&D

Sponsored by: National Materials Advisory Board, Public & Governmental Affairs Committee
Program Organizers: Toni G. Marechaux, National Research Council, National Materials Advisory Board, Washington, DC 20418 USA; Warren H. Hunt Jr., Aluminum Consultants Group Inc., Murrysville, PA 15668-2002 USA

Monday AM Room: 2009
February 14, 2005 Location: Moscone West Convention Center

Program Moderator: Warren H. Hunt Jr., Aluminum Consultants Group Inc., Murrysville, PA 15668-2002 USA

Join us for a variety of presentations and a roundtable discussion on the globalization of materials research and development. Topics and participants include:

8:30 AM
National Policy: *Toni Marechaux*[1]; [1]The National Academies, 2101 Constitution Ave. NW, Washington, DC 20418 USA

8:50 AM
Corporate Research Management: *Dianne Chong*[1]; [1]The Boeing Company, PO Box 516, St. Louis, MO 63166-0516 USA

9:10 AM
Metals Industry: *Diran Apelian*[1]; [1]Worcester Polytechnic Institute, Metal Procg. Inst., 100 Institute Rd., Worcester, MA 01609-2280 USA

9:30 AM
Electronics Industry: *Darrel Frear*[1]; [1]Freescale Semiconductor, 2100 E. Elliot Rd., Tempe, AZ 85284-1801 USA

9:50 AM Break

10:00 AM
The Role of the Materials Societies: *Brajendra Mishra*[1]; [1]Colorado School of Mines, Kroll Inst. for Extractive Metals, Dept. of Metallurgl. & Matls. Engrg., 1500 Illinois St., Golden, CO 80401-1887 USA

10:20 AM
University Perspective: *Henry Rack*[1]; [1]Clemson University, Sch. of Matls. Sci. & Engrg., 208 Rhodes Hall, Clemson, SC 29634-0921 USA

10:40 AM
Government Perspective: *Sylvia Johnson*[1]; [1]NASA Ames Research Center, USA

11:00 AM
Roundtable Discussion

Hume-Rothery Symposium: The Science of Complex Alloys

Sponsored by: Electronic, Magnetic & Photonic Materials Division, EMPMD/SMD-Alloy Phases Committee
Program Organizers: Patrice E.A. Turchi, Lawrence Livermore National Laboratory, Chemistry & Materials Science, Livermore, CA 94551 USA; Thaddeus B. Massalski, Carnegie Mellon University, Department of Materials Science and Engineering, Pittsburgh, PA 15213 USA

Monday AM Room: 3008
February 14, 2005 Location: Moscone West Convention Center

Session Chairs: Thaddeus B. Massalski, Carnegie Mellon University, Dept. of Matls. Sci. & Engrg., Pittsburgh, PA 15213 USA; Kenneth F. Kelton, Washington University, Dept. of Physics, St. Louis, MO 63130 USA

8:30 AM Opening Remarks

8:40 AM Keynote
Hume-Rothery Rule in Structurally Complex Alloy Phases: *Uichiro Mizutani*[1]; [1]Nagoya University, Dept. of Crystalline Matls. Sci., Sch. of Engrg., Furo-cho, Chikusa-ku, Nagoya 464-01 Japan

Special emphasis will be put on our understanding of why nature is able to stabilize structurally complex alloy phases like quasicrystals and gamma-brasses, the latter of which has been known as one of the typical Hume-Rothery phases for many years. Most of these structures have been synthesized by using the Hume-Rothery rule that relates fundamental aspects of electronic structure to stability. The Hume-Rothery rule related electronic structure studies on structurally complex alloy phases will be reviewed, followed by its new interpretation based on the first-principle band calculations, which hopefully goes beyond the first naive free electron picture put forward by Mott and Jones in 1936.

9:30 AM Invited
Spherical Periodicity, A General Feature of Matter at its Early Stages of Formation: *Peter Häussler*[1]; [1]Chemnitz University of Technology, Inst. of Physics, Reichenhainer Str.70, Chemnitz 09107 Germany

Structure formation, the transition from the completely disordered state to the long-ranging order of a crystal, is even for simple inorganic systems under many aspects still a mystery. Both, liquid and amorphous systems, are right on the way to form structural elements, both are precursors of the crystalline state. Understanding their fundamental structure-forming processes may once help a modern materials design. For very early stages of structure formation, within the liquid and amorphous state, local spherical periodicity around any adatom was observed due to the minimization of the total energy along a self organizing spherical-periodic resonance. The resonance arises between two macroscopic subsystems, namely the valence electrons in total as the one and the forming static structure as the other one. It is based on characteristic momenta of both subsystems and hence is a global effect. As a consequence, a pseudogap gets formed at the Fermi energy (Hume-Rothery-, Peierls-like) stabilizing the system, as well as affecting any electronic transport property. To find the optimum the forming static structure as well as the electronic system both may mutually adjust. The more degrees of freedom exist, the more optimal becomes the resonance. We are able to describe the static structure of the glassy and the liquid state of metals, ionic glasses, amorphous quasicrystals, as well as glassy semiconductors on the same roots. Due to the resonance gaps at the Fermi energy, electronic transport will strongly depend on the strength of the resonance. We propose the spherical resonance model as an autonomous missing link between the microscopic description of atoms/molecules, described by Schrödinger's equation, and the crystals where global concepts as planar resonances exist and Bloch's theorem applies. We report on different scenarios how the total system is able to optimize the resonance, give an overview on the structural features of many complex phases as liquid and amorphous systems of different type and show systematics in the structure of liquid and amorphous elements along the periodic table. Systematics in the electronic transport properties and their evolvement during the structure formation are also briefly reported.

10:00 AM Break

10:20 AM Invited
Complex Metallic Alloys: A New Frontier in Condensed Matter Physics: *Jean-Marie Dubois*[1]; [1]CNRS, LSG2M, Ecole des Mines, Parc de Saurupt, Nancy 54042 France

Aside quasicrystals, which were a focus of interest for the last two decades and obliged us to forge new tools able to solve complex crystallographic structures, many crystals based on metals present giant unit cells and intriguing properties. Whereas a few tens are known in binary compounds (e.g. Al3Mg2 with 1148 atoms per unit cell), these so-called "Complex Metallic Alloys" are supposed to be hidden in the many, as yet essentially unexplored, ternary, quaternary, etc. phase diagrams of metallic elements alloyed with metalloids and/or rare earths. The new spring board that complex intermetallics offer to metal physicists and material scientists is to understand in great detail the relationships between structural complexity and lattice and electronic excitations on the one hand and the role and nature of chemical bonding in the formation and stability of such compounds. In this respect, the seminal work of Prof. U. Mizutani on the Hume-Rothery mechanism in CMAs and quasicrystals is of key importance and wil l be illustrated by results of the author and collaborators. The talk will also put emphasis on two examples of properties, namely surface energy and reduced friction in vacuum, with a view at using selected complex metallic alloys as model systems for a deeper understanding of properties that are of technological relevance.

10:50 AM Invited
Electron Concentration Variation and Local Environment Effects in Complex Materials: *Igor A. Abrikosov*[1]; [1]Linköping University, Dept. of Physics & Measurement Tech., Campus Valla, Fysikhuset, F308, Linköping SE-58183 Sweden

The ability of the first-principles theory to describe the structural transitions in complex materials upon the change of the electron concentration will be illustrated by several examples, including the study of electronically induced phase transitions in ternary transition metal distannide systems, electronic topological transitions in Al-Zn alloys, and phase stability of Li(Mn-Co)O2 oxides. We will also reiterate that simple arguments that consider a filling of the rigid band by electrons upon alloying often fail to predict electronic and structural properties of materials. Particular attention will be paid to the so-called local environment effects, i.e. a dependence of the electronic properties of each atom in a system on its local chemical environment. We will discuss recent experimental studies where the effect is detected, and compare it with our theoretical results. Considering complex magnetic structures of Fe-Ni alloy as an example, we will show how the interplay between a change in valence electro n concentration and local environment effects can lead to a formation of a glass-like state.

11:20 AM Invited
From Electronic Structure to Phase Equilibria Calculations: *Tetsuo Mohri*[1]; Ying Chen[2]; Munekazu Ohno[3]; [1]Hokkaido University, Grad. Sch. of Engr., Div. of Matls. Sci. & Engrg., Kita-13 Nishi-8, Kita-ku, Sapporo 060-8628 Japan; [2]University of Tokyo, Dept. of Quantum Engrg. & Sys. Sci., Hongo 7-3-1, Bunkyo-ku, Tokyo 113-8655 Japan; [3]Technical University, Clausthal, Inst. fuer Metall., Robert Koch Str. 42, Clausthal-Zellerfeld D-38678 Germany

By combining electronic structure calculations with statistical mechanics calculations, phase stability and phase equilibria of a given alloy system can be predicted from the first-principles. The authors have been attempting first-principles calculations on a phase diagram for a series of Fe-based alloy systems and reproduced the transition temperature with high accuracy. Moreover, by combining with Phase Field Method, it is demonstrated that even ordering dynamics is well reproduced from the first-principles. In those calculations, Cluster Variation Method(CVM) plays a central role in evaluating a configurational free energy. The applicability of the conventional CVM, however, is limited to a system in which global lattice symmetry is preserved at each unit cell. Hence, the structural stability of a complex system such as topologically disordered systems has not been well studied by the conventional CVM. The recent progress of Continuous Cluster Variation Method (CCVM) opens up a new possibility of exploring the topological relaxations. The recent progress of the CCVM is reviewed.

Industrial Energy Reduction: Materials Opportunity Analyses

Sponsored by: TMS
Program Organizer: Sara Dillich, EERE-ITP, US Department of Energy, Washington, DC 20585 USA

Monday AM Room: 2000
February 14, 2005 Location: Moscone West Convention Center

Session Chair: Sara Dillich, EERE-ITP, US Dept. of Energy, Washington, DC 20585 USA

8:30 AM
Refractories for Industrial Processing: Energy Reduction Opportunities: James G. Hemrick[2]; *H. Wayne Hayden*[1]; Peter Angelini[2]; Robert E. Moore (Deceased)[3]; William L. Headrick[3]; [1]MMPaCT, Inc., 123 Lake Hills Dr., Oak Ridge, TN 37830-4231 USA; [2]Oak Ridge National Laboratory, Metals & Ceram. Div., PO Box 2008, MS 6069, Oak Ridge, TN 37831-6065 USA; [3]R. E. Moore and Associates, PO Box 314, Rolla, MO 67402 USA

Refractories are used in most manufacturing industries as insulation and/or containment vessel linings for high temperature and corrosive environments. In addition, refractory components often have load bearing or heat transfer functions which contribute further to their performance requirements. Reduction of energy losses and increased productivity in processing could be realized by development of higher strength refractories capable of operating at higher temperatures, development of refractories with lower thermal conductivity to reduce wall losses at higher service temperatures, improved control of thermal expansion of current refractories, and development of refractories with greater resistance to degradation. Fifteen industrial application types were analysed. Four types, boilers and reaction systems, gasifiers, reverbatory furnaces, and kilns and calciners, have been identified as areas where significant energy savings (trillions of BTUs) could be realized as a result of refractory improvement.

9:00 AM
Materials for Separations Technologies: Energy and Emission Reduction Opportunities: *William T. Choate*[1]; Robert Jubin[2]; Sharon Robinson[2]; [1]BCS, Incorporated, 5550 Sterrett Pl., Ste. #306, Columbia, MD 21044 USA; [2]Oak Ridge National Laboratory, Oak Ridge, TN USA

Separation processes are the most energy intensive industrial operations. They consume over 5,000 trillion Btu/year, more than a third of the energy consumed within manufacturing facilities. Mass transfer operations (i.e., distillation, evaporation and drying) account for 80% of the separations energy consumed. These operations are inherently high-energy consumers, utilizing "heat of vaporization" as the separating phenomena. Materials used as separation agents such as adsorbents, absorbents, ion-exchange resins, ionic liquids and membranes perform low-energy intensive "heats of solution" separations. The greatest potential for reducing industrial separations energy is the development of new and enhanced materials that will enable a shift from high-energy to low-energy technologies. Materials with improved selectivity, capacity, stability, morphology, and ability to regenerate will move these low-temperature technologies from niche applications into broader use. This study examined the largest industrial separation operations and identified over 220 trillion Btu/year of potential savings that would result from enhanced materials.

9:30 AM
Impacts of Condition Assessment on Energy Use: Selected Applications in Chemical Processing and Petroleum Refining: *Emory A. Ford*[1]; Joan Pellegrino[2]; [1]Materials Technology Institute, 1215 Fern Ridge Pkwy., St. Louis, MO 63141-6078 USA; [2]Energetics, 7164 Columbia Gateway Dr., Columbia, MD 21046 USA

Condition assessment refers to inspection of equipment for conditions such as corrosion, metal wear, and cracking. Effective methods for condition assessment of process equipment are critical to the efficient, safe operation of plants. The processes in these industries are operated at high temperatures and pressures, and in some cases in corrosive environments. Over 5 quadrillion Btu are consumed yearly in chemicals and petroleum refining for process heating and cooling. The potential for reducing energy use in two energy-intensive process applications through improved condition assessment technology is examined. The first is the ethylene cracking furnace and the second is preheat trains, used to preheat crude oil before downstream refining into products.

10:00 AM Break

10:20 AM
Energy Impacts of Corrosion: Industrial Case Studies: *Ross Brindle*[1]; [1]Energetics, Incorporated, 7164 Gateway Dr., Columbia, MD 21046 USA

Corrosion has been estimated to cost the U.S. economy over $276 billion each year. In the industrial sector alone, corrosion costs manufacturers an estimated $84 billion in the form of increased capital and operating costs, lost productivity, and lower efficiencies. Materials corrosion also leads to significant energy losses in industrial processes due to increased frequency of required shutdowns and startups, missed opportunities to capture waste heat, efficiency limitations imposed by materials performance at higher temperatures, and efficiency degradation over time. An analysis of several industrial applications indicates that the magnitude of potential energy savings associated with developing corrosion-resistant materials can be significant. Three industrial case studies have been analyzed: stress-assisted corrosion of Kraft recovery boiler tubes in pulp and paper operations, the use of recuperators in aluminum melting furnaces, and carburization of tubes in ethylene pyrolysis furnaces.

10:50 AM
Industrial Waste Heat Recovery and Reuse: *Vilayanur V. Viswanathan*[1]; James D. Holbery[1]; Richard W. Davies[1]; [1]Pacific Northwest National Laboratory, Energy Sci. & Tech. Dept., 902 Battelle Blvd., PO Box 999, MS K2-44, Richland, WA 99352 USA

This work discusses and defines the opportunities to recover energy from industrial waste heat and emissions. To evaluate these opportunities, industrial waste heat and emissions data was obtained from public, technical and business literature and publications; and analysis was performed to identify major sources of waste heat, and emissions with fuel value that might be converted into usable energy. The study was focused on the highest energy consuming industries in the U.S. - including petroleum, chemicals, forest products and primary metals industries. The amount and quality of energy available in industrial waste heat for potential recovery was characterized and quantified. The electrochemical potential and residual fuel value of industrial emissions were evaluated, and the associated energy savings, emissions reductions, and economic benefits were assessed. Major technologies, both commercial and emerging, that have high potential to recover energy from industrial waste heat and emissions will be discussed.

11:20 AM
Energy Reductions Estimated for Microchannel Technology: *Landis D. Kannberg*[1]; [1]Pacific Northwest National Laboratory, Energy Scis. Dept., PO Box 999, K9-09, Richland, WA 99354 USA

Energy reduction is one of the many benefits from utilization of microchannel architectures in systems involving heat and mass transport. Such architectures can be applied to components, systems and devices involving chemical and fuel processing, heat exchange and recuperation, and cooling and heating processes The benefits come from both fundamental improvement of process performance, as well as displacement of conventional technology with substantially different technology (enabled through process intensification achievable in microchannel architectures) that is more systemically efficient. Projected savings from such benefits, through reasonable deployment, will be provided. Finally, information on foreign investment in development of one principal area (chemical processing) will be briefly explored as an indicator of worldwide consideration of microtechnology development.

Lead Free Solder Implementation: Reliability, Alloy Development, New Technology: Interfacial Reactions and Phase Stability in Lead Free Solder Alloys

Sponsored by: Electronic, Magnetic & Photonic Materials Division, EMPMD-Electronic Packaging and Interconnection Materials Committee
Program Organizers: Mark A. Palmer, Kettering University, IMEB, Flint, MI 48504-4898 USA; Srinivas Chada, Jabil Circuit, Inc., FAR Lab/Advanced Manufacturing Technology, St. Petersburg, FL 33716 USA; Nikhilesh Chawla, Arizona State University, Department of Chemical and Materials Engineering, Ira A. Fulton School of Engineering, Tempe, AZ 85287-6006 USA; Sinn-Wen Chen, National Tsing-Hua University, Department of Chemical Engineering, Hsinchu 300 Taiwan; Sung K. Kang, IBM, T. J. Watson Research Center, Yorktown Heights, NY 10598 USA; J. P. Lucas, Michigan State University, Chemical Engineering and Materials Science, East Lansing, MI 48824 USA; Laura J. Turbini, University of Toronto, Center for Microelectronic Assembly & Packaging, Toronto, ON M5S 3E4 Canada

Monday AM Room: 3014
February 14, 2005 Location: Moscone West Convention Center

Session Chairs: Mark A. Palmer, Kettering University, IMEB, Flint, MI 48504 USA; Martin W. Weiser, Honeywell Electronic Materials, Spokane Valley, WA 99216 USA

8:30 AM Invited
Solder Thermal Interface Materials in Microprocessor Cooling: *Martin W. Weiser*[1]; Brian D. Ruchert[1]; Colin F. Edie[1]; [1]Honeywell Electronic Materials, 15128 E. Euclid Ave., Spokane Valley, WA 99216 USA

As the computational power of microprocessors grows amount of heat generated grows so that current devices generate 100W or more. This has severely strained the ability to remove the heat in a cost effective maner. One part of the solution to this problem is to reduce the thermal resistance at the interfaces between the die and the heat spreader since newer chip designs often concentrate a large portion of the heat in a small number of hot spots on the chip. Solders have traditionally been used to solve this problem in power die, but the die used in microprocessors are not as mechanically and thermally stable as power die. As a result it is necessary to to develop new solders for this application. This paper will discuss some of the issues that have arisen and been solved for indium based solders for this application.

9:00 AM
Effects of Surface Finishes on the IMC Formation and Solder Joint Reliability of Memory Module Assembly Using BGA Sn-Ag-Cu Solders: Chang Yong Park[1]; *Byung Man Kim*[1]; Dong Chun Lee[1]; Si Don Choi[1]; Joo Youl Huh[2]; [1]Samsung Electronics Co, LTD, Module Engrg. Part, Device Packing Ctr., Semiconductor Business, Asan, Chungcheongnam-do 336-711 S. Korea; [2]Korea University, Matls. Sci. & Engrg., Anam-Dong 5-1 Sungbuk-Ku, Seoul 136-701 S. Korea

Memory module involves the solder ball attachment on electronic components and the surface mount technology(SMT) of the ball grid array (BGA) components on a printed circuit board (PCB). The most widely used surface finish of the component pads is electrolytic Ni/Au, whereas organic solderability preservative (OSP) or electroless nickel with immersion gold (ENIG) is currently employed for the surface finish of the board side pads. Our previous study showed that the mechanical reliability of the component-side solder joints is largely affected by the surface finishes on the board side pads. In this work, we carried out a systematic study to identify the cause for the mechanical weakness occurring at the component-side solder joints when the OSP finish was used for the board side pads. Employing two, different solder alloys, eutectic Sn-3.5%Ag and Sn-3.0%Ag-0.5%Cu, intermetallic compounds (IMC) formed at the component-side joints during reflow, isothermal aging at 175°C, and thermal cycling were investigated for the OSP and ENIG finishes of the board-side pads. Solder joint reliability was examined by pull-off testing and bending impact testing. This talk will also discuss some remedies to improve the solder joint reliability for the case using the OSP board finish.

9:20 AM
Reliability of In-48Sn Solder/Au/Ni/Cu BGA Packages During Reflow Process: *Ja-Myeong Koo*[1]; Dae-Gon Kim[1]; Seung-Boo Jung[1];

[1]Sungkyunkwan University, Dept. of Advd. Matls., 300 Cheoncheon-dong, Jangan-gu, Suwon, Gyeonggi-do 440-746 Korea

In-48Sn solders offer low melting point and long fatigue life, so are particularly attractive for use in systems requiring low-temperature processing, such as optoelectronic devices. Interfacial reaction and ball shear properties of In-48Sn solder/Au/Ni/Cu BGA packages were investigated, to evaluate the reliability of the solder joints, during reflow process; the reflow process was performed in the reflow temperature range of 403 to 483K for 10 to 7200s in a nitrogen atmosphere. The thickness of $AuIn_2$ IMC at the interface increased during reflow process. The depletion of thin Au layer resulted the formation of Ni_3 $(Sn,In)_4$ IMC layer between the solder and Ni layer. $AuIn_2$ layer spalled away, due to the weak adhesion between $AuIn_2$ and Ni_3 $(Sn,In)_4$ layers. Shear properties decreased due to the growth and spalling of brittle $AuIn_2$ IMCs with reflow time, but increased, after 300s, due to the spalling of $AuIn_2$ IMCs and the formation of $Ni_3(Sn,In)_4$ IMC layer.

9:40 AM

Effect of Additives on Electroplating of SnAg Solder: *Hsiao-Yun Chen*[1]; Chih Chen[1]; Jia-Min Shieh[2]; Bau-Tong Dai[3]; [1]National Chiao Tung University, Dept. of Matls. Sci. & Engrg., 1001 Ta Hsueh Rd., Hsin-Chu 30050 Taiwan ; [2]National Nano Device Laboratories, 1001-1 Ta-Hsueh Rd., Hsin-Chu 30050 Taiwan

Eutectic Sn-Ag alloy solder is one of the most promising lead-free materials for low temperature processing of solder bumps on wafer. Smooth, fine-grained, and near eutectic composition (Sn-3.8 atom% Ag) of Sn-Ag alloy films could be obtained in pyrophosphate-iodide baths containing organic compounds such as PEG600 and other efficient additives by electrodeposition under both galvanostatic and potentiostatic condition. In other words, the composition of electroplated film could be controlled by optimizing with appropriate ratio of additives in main electrolytes and current density on the plating surfaces. All of the plated Sn-Ag films consisted of Ag3Sn phase, Sn, and Ag elements on a Cu foil. Electrochemical analysis such as potentiodyamic (PD) polarization was also performed to investigate the roles of these additives in electrolytes during plating. The results and mechanism will be presented in details in the conference.

10:00 AM

Wetting Properties of Lead-Free Solders: Natalie Sobczak[2]; Rafal Nowak[2]; Artur Kudyba[2]; Boris Mikulowski[3]; *Herbert Ipser*[1]; Adolf Mikula[1]; Hans Flandorfer[1]; [1]University of Vienna, Dept. of Inorganic Chmst., Waehringerstrasse 42, A-1090 Wien A-1090 Austria; [2]Foundry Research Institute, 73 Zakopianska St., Krakow PL-30418 Poland; [3]AGH University of Science and Technology, 30 Mickiewicza Ave., PL-30059 Krakow Pl-30059 Poland

The wetting and spreading behavior of different lead-free solder materials on Cu substrates was determined by a sessile drop method under different atmospheres. After these measurements, the solidified samples were cut into two halves. One part was used for push-off tests in order to determine the shear strength of the solder/substrate couple whereas the other part could be used for various metallographic investigations. Up to now, lead-free solders of the Sn-Ag-Cu, the Sn-Ag-In, and the Sn-Ag-Bi type have been investigated on Cu substrates, and the push-off tests were performed both immediately after solidification and after thermal cycling. The effect of alloying elements and testing conditions on the relationship between wetting and mechanical properties of solder/Cu model joints are discussed. It can be shown that thermal cycling changes the shear strength considerably in some instances. All the results are compared with those obtained for standard Sn-Pb solders.

10:20 AM Break

10:30 AM

Effect of Interfacial Reaction on the Tensile Strength of Sn-3.5Ag/Ni-P and Sn-37Pb/Ni-P Solder Joints: *Zhong Chen*[1]; Min He[1]; Aditya Kumar[1]; Guojun Qi[2]; [1]Nanyang Technological University, Sch. of Matls. Engrg. 639798 Singapore; [2]Singapore Institute of Manufacturing Technology, 71 Nanyang Dr. 638075 Singapore

This work investigates effect of interfacial reaction on the joint strength of two types of solder joints, Sn-3.5Ag/Ni-P and Sn-37Pb/Ni-P. Both tensile strength and fracture behavior of the joints under different thermal aging conditions have been studied. It is found that the tensile strength decreases with increasing aging temperature and duration. The decrease is due to the change in fracture behavior. Several typical failure modes have been classified. In general the failure mode shifts from within the bulk solder in the as-soldered condition toward interfacial failure modes, giving rise to the decrease of joint strength. This work also finds that for the same aging treatment, the strength of Sn-3.5Ag/Ni-P joint degrades faster than that of Sn-37Pb/Ni-P. The main cause of degradation of joint strength is found to be the microstructure change during interfacial reaction. The difference between the two types of joints can be explained by the difference in their interfacial reaction products and their growth kinetics. Current study finds there is an empirical relation between the solder joint strength and the Ni3Sn4 intermetallic compound (IMC) thickness. Therefore the IMC thickness could be used as an indication of the joint strength degradation. Kirkendall voids have been observed in the Sn-3.5Ag/Ni-P joint; however they do not appear to affect the joint strength. The volume change in Ni-P phase transformation during thermal aging generates high tensile stress inside the Ni-P layer. This stress causes mudflat cracking and delamination of the Ni-P coating from its underlying substrate after long time aging at high temperatures.

10:50 AM

Reliability of Adhesion Strength of the Sn-9Zn-1.5Ag-xBi/Cu During Isothermal Aging: *Chih-Yao Liu*[1]; Moo-Chin Wang[2]; Min-Hsiung Hon[1]; [1]National Cheng Kung University, Dept. of Matls. Sci. & Engrg., 1 Ta-Hsueh Rd., Tainan 70101 Taiwan; [2]National Kaohsiung University of Applied Science, Dept. of Mechl. Engrg., 415, Chien-Kung Rd., Kaohsiung 80872 Taiwan

The reliability of adhesion strength of the Sn-9Zn-1.5Ag-xBi/Cu during isothermal aging have been investigated. Due to the growth and decomposition of the intermetallic compounds (IMCs), the adhesion strength vary with aging 150°C from 100 to 1000 hour as wetted at 250°C for 60 s. The Cu6Sn5,Cu5Zn8 and Ag3Sn IMCs are identified at the Sn-9Zn-1.5Ag-xBi/Cu interface as aging. Fracture morphology are revealed that the fracture occured in solder matrix by sanning electron microscopy (SEM) and transmission electron microscopy (TEM) after aging. The diffusion cofficients of Sn and Zn in IMCs layer are determined at the Sn-9Zn-1.5Ag-xBi/Cu interface for aging, respectively.

11:10 AM

Effect of Flux on the Wetting Characteristics of SnAg, SnCu, SnAgBi, and SnAgCu Lead-Free Solders on Copper Substrates: Mario F. Arenas[1]; *Viola L. Acoff*[1]; [1]University of Alabama, Metallurgl. & Matls. Engrg., PO Box 870202, Tuscaloosa, AL 35487 USA

The effect of flux on the wetting characteristics of four lead-free solders namely, Sn-3.5Ag, Sn-3.5Ag-4.8Bi, Sn-3.8Ag-0.7Cu and Sn-0.7Cu, (all in wt%) on copper substrates have been studied. The fluxes investigated were rosin-nonactivated (R), rosin mildly activated (RMA), and rosin activated (RA). The wetting tests were conducted using the sessile-drop method in combination with a photographic technique that allowed a precise determination of the wetting angle. Experiments were performed at temperatures ranging from 240°C to 280°C. Results showed that fluxes significantly affect the wetting properties of the solder alloys. Contact angles ranging from 10° to 30° for RMA and between 20°-30° for RA were obtained. The use of flux R yielded larger contact angles ranging from 35° to 60°, revealing that it is not suitable as a flux for lead-free solders. The effect of temperature on contact angle depended on the type of flux used. When the temperature was increased, the contact angle decreased for fluxes RA and R. However, the use of RMA flux produced a slight increase in contact angle and in many cases the contact angle was independent of temperature. From the lead-free solders studied, Sn-3.5Ag-4.8Bi exhibited the lowest contact angles indicating improved wettability with addition of bismuth. The microstructure of the solder/copper interface was analyzed by scanning electron microscopy with energy dispersive X-ray spectroscopy. The wetting reaction of molten solder on Cu led to the formation of Cu-Sn intermetallic compounds at the solder-Cu interface. These were identified as Cu_6Sn_5 adjacent to the solder and Cu_3Sn adjacent to the substrate.

11:30 AM

Fundamental Characteristics at Sn-9Zn-1.5Ag-xBi/Cu with Precoating Sn: *Chih-Yao Liu*[1]; Moo-Chin Wang[2]; Min-Hsiung Hon[1]; [1]National Cheng Kung University, Dept. of Matl. Sci. & Engrg., 1 Ta-Hsueh Rd., Tainan 70101 Taiwan; [2]National Kaohsiung University of Applied Science, Dept. of Mechl. Engrg., 415, Chien-Kung Rd., Kaohsiung 80872 Taiwan

The fundamental Characteristics at Sn-9Zn-1.5Ag-xBi/ Cu with precoating Sn have been investigated. The intermetallic compounds (IMCs) are identified by X-ray diffraction (XRD), optical microscopy (OM), scanning electron microscopy (SEM) and energy dispersive spectrometry (EDS) as wetted at 250°C for 60 s. The wetting time and wetting force are determinded by wetting force balance. The corrosion behavior of solder alloys in 3.5 percent NaCl solution are determined by electrochemical measurements. Damage test are revealed the maximun force of Sn-9Zn-1.5Ag-xBi/ Cu with precoating Sn by dynamic mechanical analysis (DMA).

11:50 AM
The Influence of Ni3Sn4 Nanoparticles and Ni Concentration on Morphology of Sn-Ag-Ni Solders by Mechanical Alloying: *Hsiang-Yi Lee*[1]; Jenq-Gong Duh[1]; [1]National Tsing Hua University, Dept. of Matls. Sci. & Engrg., 101 Sec.2 Kuang-Fu Rd., Hsinchu 300 Taiwan

In the practice of package system, solder plays a crucial role in the interconnection of silicon die. In this study, mechanical alloying (MA) process was considered as an alternative method to produce the lead free solder pastes of Sn-3.5Ag-xNi (x=0.1, 0.5, 1.5, and 2.0). The particle size of pure-Ni doped solder was above 100μm. With increasing Ni concentration, the particle size was reduced. To reduce the particle size of SnAgNi alloys, Ni_3Sn_4 nanoparticles were doped into Sn and Ag powders to form SnAgNi composite solder. For Ni_3Sn_4-composite solder, the particle size was smaller than the pure-Ni doped solder. When the Ni_3Sn_4 concentration was low (x=0.1, 0.5), MA particles aggregated to a flat ingot with larger particle size. For higher Ni_3Sn_4 concentration (x= 1.5, and 2.0), MA particles turned to be nearly spherical with smaller particle size. The distinction of milling mechanism of Ni_3Sn_4-composite solder and the pure-Ni doped solder was discussed. Besides, the DSC results ensured the compatibility to apply the solder material for the reflow process. Wettability test also revealed that the wetting angle of Ni_3Sn_4-composite solder was smaller than the pure-Ni doped solder.

Magnesium Technology 2005: Magnesium, Primary Production and Environmental

Sponsored by: Light Metals Division, International Magnesium Association, LMD-Magnesium Committee
Program Organizers: Ramaswami Neelameggham, US Magnesium LLC, Salt Lake City, UT 84116 USA; Howard I. Kaplan, US Magnesium LLC, Salt Lake City, UT 84116 USA

Monday AM Room: 2004
February 14, 2005 Location: Moscone West Convention Center

Session Chairs: Ramaswami Neelameggham, US Magnesium LLC, Salt Lake City, UT 84116 USA; John N. Hryn, Argonne National Laboratory, Argonne, IL 60439-4815 USA

8:30 AM
Use of CO2-Snow for Protecting Molten Magnesium from Oxidation: Friedrich-Wilhelm Bach[1]; *Alexander Karger*[1]; Christoph Pelz[2]; Mirko Schaper[1]; [1]University Hanover, Inst. for Matls. Sci., Schoenebecker Allee 2, 30823 Garbsen Germany; [2]Linde Gas AG, Unterschleissheim Germany

When processing magnesium alloys, prevention of oxidation of the liquid metal is of prime importance, because of the high oxygen affinity of molten magnesium. A special danger of environmental pollution occurs from the usage of protective gases for molten magnesium. The protective gas SF6, which is widely used nowadays, increases the greenhouse effect due to it's GWP of approximately 23900 relative to CO2. At the Kyoto summit in 1997, this gas was detected as one of six gases to be restricted in use. The environmentally friendly alternatives are being examined by authors of this paper. The research goals of this group are to develop and to evaluate new methods for protecting the surface of magnesium melts. One possible alternative is covering the magnesium melt with CO2-snow. The current results will be presented in the following paper.

8:50 AM
Solid Oxide Membrane (SOM) for Cost Effective and Environmentally Sound Production of Magnesium Directly from Magnesium Oxide: *Ajay Krishnan*[1]; X. Lu[1]; U. B. Pal[1]; [1]Boston University, Dept. of Mfg. Engrg., 15 St. Marys St., Brookline, MA 02446 USA

The Solid Oxide Membrane (SOM) process is being investigated for the direct reduction of magnesium from magnesium oxide. The proof of concept for magnesium extraction by the SOM process was demonstrated earlier using a Magnesium Fluoride based flux system at 1300°C. Since the YSZ anode is the most expensive part of the system, its long-term stability is critical to the success and eventual commercialization of the SOM process. Efforts to increase membrane stability have resulted in the development of a new lower-temperature flux (1150°C). Minor additions of Yttrium-containing compounds to the flux was seen to further improve the YSZ anode stability. The results of the SOM experiments that were conducted at 1300°C and 1150°C using the old and the new flux systems, respectively, are analyzed in terms of their Faradaic efficiency, power consumption, mass-transfer characteristics and purity of magnesium produced. A preliminary cost comparison of the SOM process with the existing state of the art technology is also discussed.

9:10 AM
Wear Testing of Inert Graphite Anodes for Magnesium Production: *Boyd R. Davis*[1]; Joshua Rubenstein[2]; [1]Kingston Process Metallurgy Inc., 1102 Lancaster Dr., Kingston, Ontario K7P 1S6 Canada; [2]Queen's University, Mining Engrg., 25 Union St., Kingston, Ontario K7L 3N6 Canada

The longevity of cells requiring dimensional stability of the electrodes is limited in part because of gradual wearing of the graphite inert anodes. This wear causes increased cell resistance and hinders hydrodynamics. Preliminary scoping tests in a laboratory electrolysis cell were performed to determine whether confocal surface profilometry could be used to study anode wear. This approach provided good reproducibility, limited variation, and both quantitative and qualitative results. Oxide concentration and speciation (MgO vs. MgOHCl) in the electrolyte, as well as graphite properties, were varied to see if they could impact anode wear. Oxide speciation and concentration were found to have a direct impact on anode wear. As well, the graphite's grain size, density, and mechanical properties considerably modified the anode wear.

9:30 AM
Pilot Experiments of Magnesia Direct Electrolysis in a 10kA Magnesium Reduction Cell: *Huimin Lu*[1]; *Chunfa Liao*[1]; *Ruixin Ma*[1]; *Wenhui Yuan*[1]; [1]University of Science and Technology, Metallurgl. Engrg. Sch., No. 30 Xueyuan Rd., Beijing 100083 China

A new technique of magnesia direct electrolysis to produce magnesium with the LaCl3-MgCl2 system as support electrolyte published in Magnesium Technology 2004 has low energy consumption, high current efficiency and less pollution for the environment. In this paper, pilot experiments of the new technique of magnesia direct electrolysis in a 10kA magnesium electrolysis cell are conducted. The electrolyte is also the LaCl3-MgCl2 system. Some experiment phenomena are described. The experiment results indicate that the LaCl3-MgCl2 system is promising. These pilot experiments lay a good foundation for industrial comprehensive utilization of bischofite from Qinghai Lakes in China. In the meantime, the thermo-chemistry, electrolyte ionic species and electrode reactions of the magnesia direct electrolysis in the LaCl3-MgCl2 system are studied. The operational parameters of the new process are also compared with those of the common aluminum production process and MgCl2 electrolysis process.

9:50 AM
Electrochemical Co-Deposition of Magnesium Alloy from Alkali Chloride Melts: Xi Zhang[1]; Shuqiang Jiao[1]; *Hongmin Zhu*[1]; [1]University of Science and Technology, Dept. Physl. Chmst., 30 Xueyuan Rd., Haidian, Beijing 100083 China

A novel process is proposed for direct preparation of magnesium alloys through electrochemical co-deposition from alkali chloride molten salts with relatively lower density (i.e. LiCl~NaCl) than that of magnesium metal. According the theoretical calculation magnesium - aluminium alloy could be produced galvanosatic electrolysis at the conditions of appropriate concentration ratio of Mg2+ and Al3+ in melt. A series of electroanalytical measurements was performed for the system of MgCl2-AlCl3-NaCl-LiCl molten salts, to investigate the electrochemical behavior and basic parameters for the electrode process. A laboratory test of the direct production for the Mg-Al alloy by step-current co-deposition was also performed.

10:10 AM Break

10:25 AM
Thermal Properties of Electrolytic Magnesium Production Feed: *Muhammad R. Tawalbeh*[1]; K. W. Ng[1]; R. Harris[1]; [1]McGill University, Mining, Metals & Matls. Engrg. Dept., 3610 Univ. St., M.H. Wong Bldg., Montreal, Quebec H3A 2B2 Canada

The thermal conductivity of commercial magnesium chloride dihydrate (Prills and powdered prills) was measured at temperatures up to 200°C and of MgOHCl manufactured in house at temperatures up to 500°C as a function of porosity. It was found that the thermal conductivity of the Prills powder as a function of temperature could be represented as: k/k (298.15) =1 + 0.0015(T - 298.15) And as a function of porosity: k = 5.77*exp(- 4.47e) Furthermore, similar correlations were obtained for the MgOHCl powder in terms of the thermal conductivity, which could be represented as a function of temperature: k/k (298.15) =1 + 0.0124(T - 298.15) And as a function of porosity: k = 9.76*exp(- 2.63e) These results will facilitate the study of the thermal history of the prills in Magnola Metallurgie Inc's 'Super-chlorinator'.

10:45 AM
Protecting Liquid Mg by Solid CO2: New Ways to Avoid SF6 and SO2: *Peter Biedenkopf*[1]; Alexander Karger[2]; Michael Laukötter[4]; Willi Schneider[3]; [1]Linde AG - Linde Gas Division, Mkt. Dvlp., Carl-von-Linde-Str. 27, Unterschleissheim (Munich), Bayern 85716 Germany; [2]Universitaet Hannover, Fachbereich Technologie der Werkstoffe, Schoenebeckerallee 2, Hannover, Niedersachsen 30823 Germany; [3]Audi Ag, I/PG-63, Ingoltstadt, Bayern 85045 Germany; [4]Laukötter Gusstechnik GmbH, Krummer Weg 27-29, Wadersloh 59329 Germany

Lots of research had been done to find a new gas solution for replacing SF6 or SO2 in Mg production and processing caused by their extremely high global warming potential or toxicity. Linde Gas in cooperation with industrial and academic partners had developed a new tool for protecting liquid magnesium by covering the melt with solid CO2. Cold dry ice hinders material losses caused by oxidation and reduces also the evaporation of Mg at higher temperatures. The cooling effect of the dry ice also extinguishes fires into a furnace by cooling the surface and replacing leaking nitrogen and oxygen. Lot of work was done to reduce the CO2 consumption to make the process competitive to SF6 or SO2 operation and will be presented.

11:05 AM
Lifecycle Environmental Impact of Magnesium Automotive Components: *Paul Koltun*[1]; Ambalavanar Tharumarajah[1]; Subramania Ramakrishnan[1]; [1]CSIRO, Mfg. & Infrstuct. Tech., PO Box 56, Highett, Victoria 3190 Australia

The development of magnesium applications for automotive industries is receiving significant attention. One aspect is the assessment and reduction of the cradle-to-grave environmental impact of components. The study investigates magnesium converter housing starting from the production of magnesium ingots to the manufacture and assembly, use and recycling. Sensitivity analysis examines the impact of key parameters such as cover gases other than SF6, product yield and use of secondary magnesium, that can improve the environmental performance. Several environmental performance scenarios are proposed and used to compare the impact of similar functional components made of magnesium produced in China, aluminium and iron. The investigations shows significant reductions in the greenhouse gas impact may be achieved from the lighter magnesium components. Also, process improvements to reduce the impact improve the break-even distances in the use of automobiles at which magnesium becomes comparable with other competing metals.

11:25 AM
Mg2(OH)3Cl.2H2O Chlorination: Sina Kashani-Nejad[1]; K.-W. Ng[1]; *Ralph Harris*[1]; [1]McGill University, Mining, Metals & Matl. Engrg., 3610 Univ., Wong Bldg., Montreal, Quebec H3A 2B2 Canada

The kinetics of the hydrochlorination of Mg(OH)2Cl3 isolated form the feed of a commercial electrolytic magnesium production process, with HCl gas was investigated. It was found that particles of the isolated Mg2(OH)3Cl had an average diameter of 150 micron. Over 90% conversion to MgCl2 was observed within 30 minutes by contacting the Mg2(OH)3Cl particles with HCl gas at 350°C. Analysis of the kinetic data suggested that the chlorination process was divided into two regimes. As the chlorination process proceeds, the rate of the chlorination became controlled by the rate of HCl transfer through theMgCl2 layer formed on the Mg2(OH)3Cl core surface.

Magnesium Technology 2005: Wrought Magnesium Alloys I

Sponsored by: Light Metals Division, International Magnesium Association, LMD-Magnesium Committee
Program Organizers: Ramaswami Neelameggham, US Magnesium LLC, Salt Lake City, UT 84116 USA; Howard I. Kaplan, US Magnesium LLC, Salt Lake City, UT 84116 USA

Monday AM Room: 2006
February 14, 2005 Location: Moscone West Convention Center

Session Chairs: Howard I. Kaplan, US Magnesium LLC, Salt Lake City, UT 84116 USA; Ravi Verma, General Motors Research & Development, Warren, MI 48090-9055 USA

8:30 AM
A Comparison of the Mechanical Response High Purity Magnesium and Az31 Magnesium Alloy: *Carl M. Cady*[1]; Richard C. Korzekwa[1]; Ellen K. Cerreta[1]; Micheal F. Lopez[1]; George T. Gray[1]; [1]Los Alamos National Laboratory, MST-8, MS G-755, Los Alamos, NM 87544 USA

Constitutive property studies have been conducted on an AZ31 magnesium alloy and high purity magnesium as a function of temperature (-75°C to 200°C), strain rate (0.001 s-1 to 2500 s-1), orientation, and stress state. Minimal influence of strain rate on the yield and flow stress of this material was seen over the range of strain rates from 0.001 to 2500 s-1. Differences in the mechanical response, as a function of orientation with respect to rolling direction and stress-state, will be shown. The yield stress in the through-thickness orientation is higher than that of the in-plane direction for all strain rates. The flow stress for the in-plane orientation is initially lower than that seen in the through-thickness direction but it intersects at ~12% strain. Varying the temperature also influences the through-thickness flow stress behavior significantly more than the in-plane behavior. These differences can be attributed to the dominant deformation mechanism activated for each orientation.

8:50 AM
Magnesium Wrought Alloy Properties of the AZ - Series: *D. Letzig*[1]; J. Swiostek; J. Bohlen; J. Göken; K.U. Kainer; [1]GKSS Forschungszentrum Geesthacht GmbH, Max-Planck-Str. 1, D - 21502 Geesthacht, Germany

The alloy composition in combination with the kind of thermomechanical treatment determines the properties of magnesium semi-finished products like sheets or profiles. The development of the microstructure dependent on the process and on the chemical composition is seen as a fundamental basis for the understanding of the obtained mechanical properties. This also includes the texture development and its influence on the mechanical anisotropy of wrought alloys. The mechanical properties of different wrought alloys were determined by extrusion processes such as indirect and hydrostatic extrusion. A relationship between profile microstructure and resulting mechanical properties was investigated by also using additional methods like damping and acoustic emission measurements. In this paper an overview on the results obtained from the magnesium AZ-series will be given. They will be discussed with respect to the special needs for future developments of magnesium wrought alloys.

9:10 AM
Large Profile Magnesium Alloys Extrusions for Automotive Applications: *Gady Isaac Rosen*[1]; [1]Alubin Ltd., R&D, 36 Yosef Levi St., PO Box 1188, Kiryat Bialik, Israel 27112 Israel

The aim of this project is to develop magnesium alloys extrusion technology for large profiles for application in the automotive industry. In particular it is expected to significantly reduce Chassis weight, thus leading to fuel consumption reduction and enhancement of performance of the cars produced by the end user. The entire process required for magnesium alloys extrusion of automobile Chassis will be addressed as a first attempt of large magnesium profile extrusion. The challenge of large magnesium profile extrusion (outer diameter up to 10") has never been addressed due to technological barriers that relate to limited capability of magnesium extrusion technology. However, these barriers can be overcome if one has control over the starting material. Since the final performance of the finished product depends on the original microstructure formed over Direct Chill (DC) casting, homogenization, extrusion and heat treatment, no processing step can be isolated from the other. The R&D activities will focus on alloy selection, production of large magnesium billets, die design, heat treatment and extrusion parameters. These will be accompanied by an economic assessment of the new technology and additional applications.

9:30 AM
Microstructure Refinement of Magnesium Alloy (AZ31) Through a Combination of Extrusion and Room Temperature Equal Channel Angular Process: *Jeong-Whan Han*[1]; [1]INHA University, Sch. of Matl. Sci. & Engrg., Inchon 402-751 Korea

In order to obtain ultra fine microstructures of magnesium alloy (AZ31), a new processing procedure was applied to Mg-3wt.%Al-1wt%Zn alloy. This procedure involves the sequential application of hot extrusion and equal-channel angular pressing at room temperature. The AZ31 alloy was extruded to a billet with a thickness of 5mm, and then ECA Pressing was carried out at room temperature on the as-extruded material through a die with an internal angle(¥Õ) of 135 between the vertical and horizontal channels and a curvature angle(¥×) of 45. For the ease of room temperature ECAP, heat treatment of extruded slab was carried out at a temperature of 623K. Experiments show that the magnesium alloy(AZ31) has an initial grain size of about 90§- after casting and it is further reduced to about 2§- when the extruded alloy is subjected to ECAP at room temperature(298K). A

combination processing of extrusion and room temperature ECA Pressing using magnesium alloy suggested a application as structural material because microstructure was refined by severe plastic deformation just like extrusion under high extrusion ratio followed by a shear deformation by means of room temperature ECA Pressing without grain growth.

9:50 AM
Measuring the Temperature Dependence of the Flow Surface of Magnesium Alloy Sheet: *Ashutosh Jain*[1]; Sean R. Agnew[1]; [1]University of Virginia, Matls. Sci & Engrg., 116 Engineer's Way, Charlottesville, VA 22904 USA

The present study attempts at characterizing the anisotropic behavior of the Mg AZ31B sheet alloy and constructing a flow surface using minimum possible experimental data. Uni-axial tests in compression and tension were conducted at room temperature and at elevated temperatures to measure the strain anisotropy at various strain levels. The true-stress true-strain curves at room temperature show that the material is soft during in-plane compression and then strain hardens rapidly at å >0.05. Compression in the normal direction is observed to be the typical parabolic hardening curve. With an increase in temperature, the steep hardening in the RD and TD compression decreases and finally vanishes at T ~ 150°C even though the strain anisotropy is significant at this temperature. The flow stresses at different strains were used to construct flow surfaces, at different temperatures. Finally, a visco-plastic self-consistent approach was used to model the deformation behavior and simulate a poly-crystal yield sur face at room temperature. The model was fit using the RD tensile flow stress and strain anisotropy.

10:10 AM Break

10:25 AM
High Strength Wrought Magnesium Alloys in Employing Grain-Refined Powder: *Katsuyoshi Kondoh*[1]; [1]University of Tokyo, Rsch. Ctr. for Advd. Sci. & Tech., 4-6-1, Komaba, Muguro-ku, Tokyo 153-8904 Japan

Magnesium alloy powder with fine grains less than 5 ìm was produced via continuously direct plastic working on coarse raw powder with 1~4mm length. Dynamic recrystallization of the matrix grains during the warm plastic working causes the refinement of grains and the drastic hardening. When optimizing the process parameters of the plastic working, AM60 wrought alloy after hot extrusion shows UTS of 380MPa and 6% elongation at room temperature. It reveals uniformly refined microstructure, in particular the mean grain size of 1.4 ìm.

10:45 AM
Microstructure Control of AZ31 Alloys by Different-Speeds-Rolling and the Formability: *Tsunemichi Imai*[1]; Naobumi Saito[1]; Ichinori Shigematsu[1]; Kazutaka Suzuki[1]; Shangli Dong[2]; [1]National Institute of Advanced Industrial Science & Technology, Matls. Rsch. Inst. for Sustainable Dvlp., 2266-98 Shimoshidami, Moriyama-ku, Nagoya 463-8560 Japan; [2]Harbin Institute of Technology, Sch. of Matls. Sci. & Engrg., PO Box 432, Harbin 150001 China

AZ31 alloys processed by different-speeds-rolling (DSR) have relatively uniformly fine grain size of 10~20mm and strong anisotropy of mechanical properties by texture built during DSR processing. And, the AZ31 rolled with the billet temperature of 623K and roller of room temperature produces anisotropy in superplastic elongation at the strain rate of 10-2 s-1 and 723K. Conical Cup Testing and Blow Forming of the AZ31 processed by DSR are performed to make clear the Formability.

11:05 AM
Effect of Strontium on the Microstructure and Mechanical Properties of AZ31 Magnesium Alloy: *Yingxin Wang*[1]; Xiaoqin Zeng[1]; Wenjiang Ding[1]; *Alan Luo*[2]; Anil K. Sachdev[2]; [1]Shanghai Jiao Tong University, Natl. Engrg. Rsch. Ctr. of Light Alloys Net Forming, Huashan Rd. 1954, Shanghai, Shanghai 200030 China; [2]General Motors Research and Development Center, Matls. & Processes Lab., 30500 Mound Rd., Warren, MI 48090-9055 USA

The effect of strontium on the microstructure and mechanical properties of AZ31 magnesium alloy, and the sensitivity to section thickness of the grain refinement are investigated. Three phases, block-shaped Mg17Al12, acicular Mg20Al20Mn5Sr and insular Mg16(Al,Zn)2Sr are identified in the Sr-containing AZ31 alloys. The results show that, with reducing section thickness, the amount of block-shaped Mg17Al12 phases increases, but acicular Mg20Al20Mn5Sr phases diminish and insular Mg16(Al,Zn)2Sr phases are refined and granulated. The study suggests that the grain size decreases with the reducing section thickness at a given composition, while the grain size decreases first, then increases and finally decreases again with increasing Sr content at a given section thickness. The mechanical properties of AZ31 magnesium alloy are improved by the Sr grain refinement, and the yield strength (sy) can be expressed as a function of the grain size (13d-1/2) according to the Hall-Patch relationship sy=35.88+279.13d-1/2.

11:25 AM
Grain Refinement of Wrought AZ61 Magnesium Alloy: Zhou Haitao[1]; Liu Chuming[2]; Ding Wenjiang[1]; [1]Shanghai Jiaotong University, Sch. of Matls. Sci. & Engrg., 1954 Huashan Rd., Shanghai 200030 China; [2]Central South University, Sch. of Matl. Sci. & Engrg., Hunan Changsha, Changsha 410083 China

Deformation behaviors of AZ61magnesium alloy during hot compression at temperature range from 523 K to 673 K and strain rate from 0.001s-1 to 1 s-1 were investigated. Dynamic recrystallization took place, and grains could be greatly refined through dynamic recrystallization. The mean size of the recrystallized grains decreased with the decrease of temperature or the increase of Z (Zener-Hollomon parameter), while the reciprocal of the recrystallized grains had a good linear relationship with the natural logarithm of Z value. The fine grain microstructure of extruded AZ61 magnesium alloy between 10-25µm were observed at the lower deformation temperature of 523-623K by means of the relationship between d and Z parameter.

11:45 AM
Investigation of Low Temperature Superplasticity on Mg-AZ31B Sheet: *Ozgur Duygulu*[1]; Sean R. Agnew[1]; [1]University of Virginia, Matls. Sci. & Engrg., Charlottesville, VA 22904 USA

Mechanical properties and low temperature superplasticity of commercial magnesium alloy AZ31B sheet is investigated by tensile tests at temperatures between room temperature and 200°C. In order to examine the low temperature superplasticity of magnesium alloy, tensile tests are performed at elevated temperatures at initial strain rates between $1x10^{-4}$ and $1x10^{-1}$ s^{-1}. Strain rate jump tests are also performed at true strain rates between $5x10^{-7}$ and $5x10^{-2}$ s^{-1}. Strain rate sensitivity is found to be less than 0.2 at 200°C for strain rates higher than $5x10^{-5}$ s^{-1}. Even though strain rate sensitivity is low, respectable ductility is observed with elongations up to 250%.

Materials Processing Fundamentals: Solidification & Casting

Sponsored by: Extraction & Processing Division, Materials Processing & Manufacturing Division, EPD-Process Fundamentals Committee, MPMD/EPD-Process Modeling Analysis & Control Committee
Program Organizers: Princewill N. Anyalebechi, Grand Valley State University, Padnos School of Engineering, Grand Rapids, MI 49504-6495 USA; Adam C. Powell, Massachusetts Institute of Technology, Department of Materials Science and Engineering, Cambridge, MA 02139-4307 USA

Monday AM Room: 3001
February 14, 2005 Location: Moscone West Convention Center

Session Chair: Prince N. Anyalebechi, Grand Valley State University, Padnos Sch. of Engrg., Grand Rapids, MI 49504-6495 USA

8:30 AM
Modeling the Effects of Internal Convection on Dendritic Evolution in Stainless Steel Alloys: *Alaina B. Hanlon*[1]; Robert W. Hyers[1]; Douglas M. Matson[2]; [1]University of Massachusetts, Dept. of Mechl. & Industl. Engrg., Engrg. Lab Bldg., 160 Governors Dr., Amherst, MA 01003 USA; [2]Tufts University, Dept. of Mechl. Engrg., Rm. 025 Anderson Hall, 200 College Ave., Medford, MA 02155 USA

Certain Fe-Cr-Ni stainless steel alloys solidify from an undercooled melt by a 2-step process in which the metastable ferrite phase transforms to a stable austenite phase. Recent experiments have shown that the lifetime of the metastable phase is strongly influenced by flow within the molten sample. The current research will provide insight to why flow affects the metastable phase. This will lead to the use of convection to control microstructural evolution and advancements in spray-forming of stainless steels. Simulations using a commercial computational fluid dynamics package, FIDAP, yield a range of convective flow velocities that cause mechanical damage to the dendrites and are compared to experimental results. If the convective velocities are great enough such that the dendrites bend then low angle boundaries

form at the points of collision. These result in high energy sites that could serve as nuclei for the stable phase.

8:55 AM
Predictions of Segregation Related Defects in Vacuum Arc Remelting of Titanium Alloys: *Kent J. VanEvery*[1]; Matthew John M. Krane[1]; [1]Purdue University, Matls. Engrg., 501 Northwestern Ave., W. Lafayette, IN 47907-2044 USA

Macrosegregation during vacuum arc remelting (VAR) of a wrought titanium alloy (Ti-10-2-3) has been modeled. Features of the macroscopic model include species transport and DC electromagnetic effects coupled with fluid flow, heat transfer, and solidification. The effects of different melt histories and hot top procedures on predicted macrosegregation patterns, local solidification times, and liquid pool profiles are demonstrated. Changes in the ingot radius and height, as well as the current distribution into the melt pool, are evaluated. The triple melt of an ingot is also modeled, with the segregation in a given stage affecting the input of metal into the downstream stages. The triple melt results are compared to the segregation levels for a single melt with a homogeneous electrode.

9:20 AM
Inverse Algorithm for Parameter Identification and Process Design in Materials Processing: *Kei Okamoto*[1]; *Ben Q. Li*[1]; [1]Washington State University, Sch. of Mechl. & Matls. Engrg., PO Box 642920, Pullman, WA 99163 USA

This paper discusses the parameter identification and process design for solidification processing systems using the inverse methods. The inverse algorithm entails the use of the Tikhonov regularization method, along with the L-curve method used to select optimal regularization parameters for inverse calculations. The algorithm development and its application to determine material property parameters and to the design of materials processing systems are discussed. The inverse identification of diffusivity data from experimental measurements is discussed. The design algorithm also is applied to determine the appropriate boundary heat flux distribution in order to obtain a unidirectional solidification front in a 2-D cavity by eliminating the effect of natural convection. Inverse calculation is also performed for the case in which the solid-liquid interface is prescribed by a process designer.

9:45 AM
Effect of Dendrite Coarsening and Back Diffusion on Macrosegregation in a Solidifying Alloy: *Deep Samanta*[2]; Nicholas Zabaras[1]; [1]Cornell University, Matls. Process Design & Control Lab., Sibley Sch. of Mechl. & Aeros. Engrg., 188 Frank H.T. Rhodes Hall, Ithaca, NY 14853 USA; [2]Cornell University, Matls. Process Design & Control Lab., Sibley Sch. of Mechl. & Aeros. Engrg., 169 Frank H.T. Rhodes Hall, Ithaca, NY 14853-3801 USA

Solidification of an alloy is invariably accompanied by redistribution of solute on both macro and micro length- scales. Microsegregation, which refers to distribution of solute on a length scale of secondary dendrite arms spacings, influences the underlying microstructure of a cast alloy. This in turn affects final mechanical properties of the alloy. Two limits of microsegregation are the Lever rule (infinitely fast back diffusion) and Scheil rule (no back diffusion). Under the assumption of equilibrium at the solid-liquid interface, solute redistribution with a finite amount of back diffusion occurs between these two limits. Dendrite coarsening also affects solute redistribution. It has been shown to bridge differences in microsegregation predicted by the two limiting models even under equilibrium conditions. Our main aim is to incorporate dendrite coarsening, back diffusion and interfacial transport mechanisms into an alloy solidification model where the governing equations of fluid flow, heat and solute transport are based on volume averaging. This composite model will then be used to study effects of both these mechanisms on macrosegregation in a solidifying alloy. Macrosegregation predictions from here will be compared with those obtained using Scheil and Lever rule models in the presence of convection. Simulations will be carried out using a stabilized finite element model for solidification developed recently and both two and three dimensional examples will be considered.

10:10 AM Break

10:25 AM
Numerical Simulation and Experimental Characterization of a Binary Aluminum Alloy Spray - Application to the Spray Rolling Process: *Samuel B. Johnson*[1]; Jean-Pierre Delplanque[1]; Yaojun Lin[2]; Yizhang Zhou[2]; Enrique J. Lavernia[2]; Kevin M. McHugh[3]; [1]Colorado School of Mines, Div. of Engrg., 1610 Illinois St., Golden, CO 80401 USA; [2]University of California, Dept. of Cheml. Engrg. & Matls. Sci., Coll. of Engrg., One Shields Ave., Davis, CA 95616 USA; [3]Idaho National Engineering and Environmental Laboratoty, Industl. & Matl. Techs. Dept., PO Box 1625, Idaho Falls, ID 83415 USA

A stochastic, droplet-resolved model has been developed to describe the behavior of a binary aluminum alloy spray during the spray rolling process. In this process, a molten aluminum alloy is atomized and the resulting spray is deposited on the rolls of a twin-roll caster to produce aluminum strip. The one-way coupled spray model allows the prediction of spray characteristics such as enthalpy and solid fraction and their distribution between the nozzle and the deposition surface. This paper outlines the model development and compares the predicted spray dynamics to PDI measurements performed in a controlled configuration. Qualitative comparisons are also made with the observed behavior of the spray rolling process.

10:50 AM
The Recrystallisation and Texture in Strip Cast Low Carbon Steel: *Wanqiang Xu*[1]; Michael Ferry[1]; [1]University of New South Wales, Sch. of Matls. Sci. & Engrg., Sydney, NSW 2052 Australia

Direct strip cast steel is being commercialised because of its low cost. The formability of strip cast low carbon steel, mainly depended on the texture components, needs to be improved through thermal mechanical processing. Four microstructures -acicular ferrite, bainite, fine polyganol ferrite and coarse polyganol ferrite, can be formed in strip casting low carbon steel. Fours kinds of specimens with the above imitated microstructures and one kind of direct strip cast specimen with acicular ferrite, were cold rolled at a reduction rate 50%, 70% and 90% respectively. All of the cold rolled specimens were annealed at 580, 600, 620 and 640°C in lead bath. The recrystalisation behaviour and texture in the annealled specimen were analysed.

11:15 AM
Microstructural Evolution and Deformation Behavior of Austenitic Stainless Steel in Semi-Solid State: *Jingyuan Li*[1]; [1]University of Tokyo, Inst. of Industl. Sci., Komaba 4-6-1, Meguro-Ku, Tokyo 153-8505 Japan

Thixoforming or Semi-Solid Metal Forming offers many advantages in comparison with casting and conventional forging. The purpose of the present study is to provide the basic microstructure and deformation data for austenitic stainless steel under mushy state. As well known, the alloys in Fe-Cr-Ni ternary system solidify in different modes according to the different position in the phase diagram. In this paper, microstructural evolutions of three kinds of austenitic stainless steel, which solidify in different modes, are investigated during partial remelting by way of SIMA (Strain Induced Melted Activation). Also, hot compression tests of these alloys for varied combination of deformation rate and deformation temperature in semi-solid state are conducted. Flow stress curves exhibit abrupt change according to the difference in inner microstructure. Phase segregation, fracture and deformation of solid particles are observed after compression tests. Last, various deformation mechanisms are proposed for various microstructures.

11:40 AM
Investigation of the Effects of As-Cast Microstructure and Temperature on the Response of Aluminum Alloy 3004 Ingots to Homogenization: *Prince N. Anyalebechi*[1]; [1]Grand Valley State University, Sch. of Engrg., L. V. Eberhard Ctr., Ste. 718, Grand Rapids, MI 49504-6495 USA

The effects of the fineness of as-solidified cast microstructure and temperature on the response of aluminum alloy 3004 to homogenization heat treatment have been investigated. The study was conducted on directionally solidified laboratory-size ingots with a range of solidification rate of 0.10 K/s to 30 K/s, at 811-868 K. Optical and electron microscopy, quantitative image analysis, electrical conductivity, and electron probe microanalysis were used to quantify the effects of homogenization on the microstructure of aluminum alloy 3004. In general, increase in fineness of as-cast microstructure and homogenization temperature enhanced the alpha-transformation reaction, dissolution of Mg2Si, elimination of dendritic microsegregation, and dispersoid formation. Homogenization reduced the average size of second phase particles in ingots solidified at <1 K/s. However, in ingots solidified at above 1 K/s, homogenization caused the coarsening of the second phase particles. Mn in solid solution was independent of homogenization heat treatment temperature.

Mechanical Behavior of Thin Films and Small Structures: Strengthening Mechanisms at Small Length Scale

Sponsored by: Structural Materials Division, SMD-Mechanical Behavior of Materials-(Jt. ASM-MSCTS), MPMD-Nanomechanical Materials Behavior

Program Organizers: Xinghang Zhang, Texas A&M University, Department of Mechanical Engineering, College Station, TX 77843-3123 USA; Brad L. Boyce, Sandia National Laboratories, Materials and Processes Sciences Center, Albuquerque, NM 87185 USA; Evan Ma, Johns Hopkins University, Department of Materials Science & Engineering, Baltimore, MD 21218 USA; Andrew Minor, Lawrence Berkeley National Laboratory, National Center for Electron Microscopy, Berkeley, CA 94720 USA; Christopher L. Muhlstein, Pennsylvania State University, Department of Materials Science & Engineering, University Park, PA 16802 USA; Judy A. Schneider, Mississippi State University, Department of Mechanical Engineering, Mississippi State, MS 39762 USA

Monday AM Room: 2024
February 14, 2005 Location: Moscone West Convention Center

Session Chairs: Xinghang Zhang, Texas A&M University, Dept. Mechl. Engrg., College Sta., TX 77843-3123 USA; Richard G. Hoagland, Los Alamos National Laboratory, Matls. Sci. & Tech. Div., Los Alamos, NM 87545 USA

8:30 AM Opening Remarks: Welcome and Overview of the Symposium

8:35 AM Invited
Shear of Weak Interfaces as a Strengthening Mechanism in Nanoscale Layered Composites: *Richard G. Hoagland*[1]; John P. Hirth[1]; [1]Los Alamos National Laboratory, Matls. Sci. & Tech. Div., MS G755, Los Alamos, NM 87545 USA

In layered composites containing incoherent interfaces, such as those formed from metals with dissimilar crystal structure or large lattice parameter mismatch, coherency stresses are unlikely as a source of resistance to slip. However, when the layer thicknesses are reduced to a few nanometers, these materials, e.g., Cu/Nb, achieve very high strength levels. Atomistic simulations of an fcc/bcc system containing incoherent interfaces, reveals that such interfaces will shear in response to the stress fields of nearby dislocations. We present these results and show their implications that: 1) dislocations near such interfaces are attracted to them, 2) available glide dislocation densities are reduced or eliminated as the layer thickness is reduced and 3) once they enter an interface the cores of the dislocatios spread. Both consequences make it difficult for slip to tranfer across the interface and we suggest that this behavior can explain the origins of strength in systems with incoherent interfaces. We also de scribe a linear elastic model of a dislocation interacting with shear cracks created on a weak interface that helps to generalize the results to enable predictions of the relation of interfacial shear strength to the overall strength of this type of composite. This work was supported by the Office of Basic Energy Sciences, U. S. Dept. of Energy.

9:00 AM
Mechanical Behavior of Nanolayered Laminated Composites: X. Deng[1]; C. Cleveland[1]; M. Koopman[2]; T. N. Lin[3]; Y. Y. Hsieh[3]; N. Chawla[1]; *K. K. Chawla*[2]; J. P. Chu[3]; [1]Arizona State University, Dept. of Cheml. & Matls. Engrg., Fulton Sch. of Engrg., Tempe, AZ 85287-6006 USA; [2]University of Alabama, Dept. of Matls. Sci. & Engrg., Birmingham, AL 35209 USA; [3]National Taiwan Ocean University, Inst. of Matls. Engrg., Keelung 202 Taiwan

Small-length scale multilayered structures are attractive materials because of their extremely high strength and flexibility, relative to conventional laminated composites. In this talk we present results on nanolayered laminated composites of Al and SiC. The laminated composites were fabricated by physical vapor deposition (magnetron sputtering) of alternate layers of Al and SiC. The microstructure of the multilayered structures was characterized by transmission electron microscopy (TEM). The mechanical properties of the layered materials were characterized by nanoindentation and tensile testing. Tensile testing was conducted on a high-resolution micromechanical testing system. The influence of layer thickness on hardness and Young's modulus of individual layers was quantified. The Young's modulus and tensile strength of the composites were also measured. Comparison of experimentally-determined Young's modulus with predictions from analytical models will be presented. Finally, a comparison of tensile strength of the composite with that of monolithic materials, as well as differences in fracture behavior will be discussed.

9:15 AM
Strength of Metallic Multilayers at All Length Scales Via a Dislocation-Based Model: *Lei Fang*[1]; Lawrence H. Friedman[1]; [1]Pennsylvania State University, Dept. of Engrg. Sci. & Mech., 212 Earth & Engrg. Sci. Bldg., Univ. Park, PA 16802 USA

Metallic multilayers can be used as ultra-high strength coatings. They exhibit a very strong Hall-Petch-like size-effect where the mechanical strength depends on layer thickness. At large length scale, the behavior of multilayers can be described by scaling laws (Friedman and Fang, TMS Letters, 1:3, 2004). At small length scales, discreteness of dislocations becomes important, and large deviation from the scaling law occurs. A complete analytic model should apply at all length scales. A dislocation-based model is constructed analytically for the very large and very small length scales. Combining these solutions, an analytic formula that spans the entire length scale range is obtained. The consequences to the multilayer deformation map (Misra, et al., Script Mat., 41(9): 973, 1999) are also discussed. The model is applied to Cu/Ni multilayers.

9:30 AM Invited
Nano-Structured Ultra-Hard Al-Si Films Synthesized by High Rate Deposition: Velimir Radmilovic[1]; *David Mitlin*[2]; Ulrich Dahmen[1]; [1]Lawrence Berkeley National Laboratory, University of California, NCEM, MS-72, 1 Cyclotron Rd., Berkeley, CA 94720 USA; [2]University of Alberta, Cheml. & Matls. Engrg., Edmonton, Alberta T6G 2G6 Canada

We used high rate electron-beam co-evaporation to synthesize Al-Si thin films displaying remarkable mechanical properties. The composition of these films was varied from 2 to 23at.%Si. These films were compared with pure Al films grown using identical deposition conditions to be studied as a baseline. With increasing Si content the nano-indentation hardness increased from 1 GPa for the pure Al film to 4 GPa for the film containing 30at.% Si. Analysis of the indents indicated that all samples exhibited plasticity during deformation. We analyzed the films' microstructure using conventional, atomic resolution and analytical transmission electron microscopy. The microstructure of the alloy films was an order of magnitude finer than that of pure Al, with grain sizes in the range from tens to several hundreds of nanometers. The Si grains were multiply twinned, whereas as expected the Al grains were twin-free. In addition, the Si concentration in the Al grains was consistently measured to be well above the equilibri um room temperature composition. This work was supported by the Director, Office of Science, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

9:55 AM
Mechanical Characterization of Nanoporous Zeolite Low-k Thin Films: *Junlan Wang*[1]; Lili Hu[1]; Yushan Yan[2]; [1]University of California, Dept. of Mechl. Engrg., Riverside, CA 92521 USA; [2]University of California, Dept. of Cheml. & Environml. Engrg., Riverside, CA 92521 USA

Zeolites are a class of inorganic crystalline oxides with uniform molecular-sized pores (0.3 - 2nm). Nanoporous zeolite thin films have been demonstrated to be a promising candidate for low-k applications. A key advantage of zeolite-based low-k materials is the ability to lower k while maintaining higher mechanical strength than other amorphous porous low-k materials. With the rapid development in the synthesis process of different zeolite thin films and the evaluation of their electrical and chemical functions, characterizations of the mechanical and interfacial properties have also been brought to demand. During the integration process of low-k films with other semiconducting materials, mechanical and interfacial strength of the film plays an important role in controlling the later performance and lifetime of the integrated devices. In this work, depth sensing nanoindentation and laser induced thin film spallation techniques are used to evaluate the mechanical and interfacial properties of zeolite thin film s on Si substrates synthesized with different hydrothermal methods. The results provide meaningful guidelines for the optimization of zeolite thin film synthesis processes.

10:10 AM Break

10:25 AM Invited
Mechanical Properties of Copper with Nano-Scale Twins: L. Lu[1]; Y. F. Shen[1]; *K. Lu*[1]; [1]Chinese Academy of Sciences, Inst. of Metal Rsch., Shenyang Natl. Lab. for Matls. Sci., Shenyang 110016 China

Significantly increasing the number of grain boundaries (GBs) by grain refinement in polycrystalline metals into the nanometer scale leads to a substantial change in mechanical properties. Similarly, it is interesting to learn the mechanical behaviors of polycrystalline metals in which a high density of twin boundaries (TBs) are introduced, esp. when the twin lamella thickness is the nanometer regime. By using the pulsed electro-deposition technique, a pure Cu sheet was synthesized with a unique microstructure: a high density of twins with nano-scale thickness confined in submicron-sized grains. Mechanical properties of the the as-deposited sample were investigated by means of tensile tests and nanoindentation measurements. An extremely high tensile strength up to 1 GPa with an elongation-to-failure of 13.5% was observed. The plastic deformation mechanism and the effect of a high density of TBs on mechanical properties will be discussed in terms of microstructural observations and measurement results of the strain rate sensitivity.

10:50 AM
Grain-Boundary Relaxation in Nanocrystalline Fe and its Effect on the Mechanical Behavior: Dongchan Jang[2]; *Michael Atzmon*[1]; [1]University of Michigan, NERS & MSE, Cooley Bldg., 2355 Bonisteel Blvd., Ann Arbor, MI 48109-2104 USA; [2]University of Michigan, Dept. of MSE, 3062 H. H. Dow, 2300 Hayward, Ann Arbor, MI 48109-2136 USA

Extensive plastic deformation, e.g., by mechanical attrition, can result in grain diameters as small as 10 nm. The dependence of the mechanical behavior on the grain size in this regime has been studied extensively. However, the mean grain diameter is not the only parameter that determines the mechanical behavior. In the present study, we have investigated the structure and mechanical behavior of nanocrystalline Fe formed by ball milling. The mean grain size has been characterized by the Warren-Averbach method and confirmed by transmission electron microscopy (TEM). Following low-temperature thermal treatment that does not affect the grain size or the hardness, we observe significant changes in the strain-rate sensitivity. The evolution is similar at different annealing temperatures, but its rate is temperature dependent. A likely explanation of this behavior is based on nonequilibrium structure of or impurity redistribution at the grain-boundaries. In this paper, both possibilities are addressed using high-resolution TEM.

11:05 AM
The Influence of Grain Size on Mechanical Behaviors in Nanostructured Metals: *Hongqi Li*[1]; Fereshteh Ebrahimi[2]; [1]University of Tennessee, Matls. Sci. & Engrg. Dept., Knoxville, TN 37996 USA; [2]University of Florida, Matls. Sci. & Engrg. Dept., Gainesville, FL 32611 USA

Based on the hardness measurement and computer simulation results, there generally is a strongest grain size. That is, the strength of nanocrystalline materials starts to decrease with further decreasing the grain size when the grain size is below a critical value. Furthermore, computer simulation reveals that the deformation mechanisms are different below and beyond this critical value. In current study, the tensile behaviors of nanocrystalline nickel and nickel-iron alloys were investigated to characterize how they change with the grain size.

11:20 AM Invited
Yield of Gold Nanowires: *Ken Gall*[1]; Jiankuai Diao[1]; Martin L. Dunn[1]; [1]University of Colorado, Dept. of Mechl. Engrg., Boulder, CO 80309 USA

Strength is one of the most fundamental and significant mechanical properties of a material; it measures the basic capability to bear load. The yield, or fracture, of a metal results in a decrease, or complete loss, of load bearing capacity and, in most cases, loss of functionality. We use atomistic simulations to systematically investigate the strength of experimentally observed gold wires that span atomic and nanometer size scales. The atomistic predictions of strength are quantitatively consistent with discrete experimental observations at extreme size scales and they reveal, for the first time, the mechanisms for increasing nanowire strength with decreasing dimensional scale. At nanometer scales, the mechanism for strengthening involves the scarcity and low mobility of dislocations coupled with constraint from tensile surface stresses. As the wires approach the atomic, or sub-nanometer scale, a sharp increase in strength occurs commensurate with a change in the stable structure of the nanowires and a disappearance of dislocation-mediated yield. The results constitute a new fundamental understanding of the yield behavior of low-dimension metallic wires.

11:45 AM
Mechanical Properties of GaN and ZnO Nanowires Using Nanoindentation: *Gang Feng*[1]; Youngki Yong[2]; Cheol Jin Lee[3]; Kyeongjae Cho[2]; William D. Nix[1]; [1]Stanford University, Matls. Sci. & Engrg., 416 Escondido Mall, Bldg. 550, Stanford, CA 94305 USA; [2]Stanford University, Mechl. Engrg., Durand Bldg., 496 Lomita Mall, Stanford, CA 94305 USA; [3]Hanyang University, Dept. of Nanotech., 17 Haengdang-dong, Seongdong-Gu, Seoul 133-791 Korea

Interest in the mechanical properties of nanowires is related to the large strains that can exist in these materials and the electronic effects of such strains. Because of the small dimensions, nanoindentation is a useful technique for the study of their mechanical properties. In this work, the mechanical properties of GaN and ZnO nanowires have been studied using the Nanoindenter XP™ with image scanning capability. To minimize the uncertainty in determining the contact area, the true hardness (H_t) is used, HM^2/E^2. Here, H and E are the Oliver-Pharr hardness and Oliver-Pharr reduced modulus, respectively; M is the calculated reduced modulus based on the bulk properties of the materials under study. We found that H_t remains constant while H scatters significantly. Since the geometry of the indentation of nanowires differs from that for the indentation of a half space, a new model is provided to analyze for this effect.

12:00 PM
Anomalies in Stiffness and Damping of a 2D Discrete Viscoelastic System Due to Negative Stiffness Components: *Yun-Che Wang*[1]; John G. Swadener[1]; Roderic S. Lakes[2]; [1]Los Alamos National Laboratory, MST-8, MS G755, Los Alamos, NM 87545 USA; [2]University of Wisconsin, Dept. of Engrg. Physics, 1500 Engrg. Dr., 146 Engrg. Rsch. Bldg., Madison, WI 53706 USA

The recent development of using negative stiffness inclusions to achieve extreme overall stiffness and mechanical damping of composite materials reveals a new avenue for constructing high performance materials. One of the negative stiffness sources can be obtained from phase transforming materials in the vicinity of their phase transition, as suggested by the Landau theory. To understand the underlying mechanism from a microscopic viewpoint, we theoretically analyze a 2D, nested triangular lattice with pre-chosen elements containing negative stiffness to demonstrate anomalies in overall stiffness and damping. Combining with current knowledge from continuum models, based on the composite theory, such as the Voigt, Reuss, and Hashin-Shtrikman model, we further explore the stability of the system with Lyapunov's indirect stability theorem. The evolution of the microstructure in terms of the discrete system will be discussed. A potential application of the results presented here is to develop special thin films with unusual in-plane mechanical properties.

12:15 PM
Investigation of Size Effects in the Mechanical Behavior of FCC Bicrystals by Quasicontinuum Method: *Frederic Sansoz*[1]; Jean-Francois Molinari[2]; [1]University of Vermont, Dept. of Mechl. Engrg., 33 Colchester Ave., Burlington, VT 05405 USA; [2]Johns Hopkins University, Dept. of Mechl. Engrg., Latrobe Hall, Baltimore, MD 21218 USA

Grain boundary deformation mechanisms play an important role on the onset of crystal lattice plasticity and cooperative grain behavior in nanocrystalline films and coatings at room temperature. Only the relevant information obtained from atomic scale processes at the boundaries, however, should be taken into account in order to address the challenge of scales involved in the hierarchical modeling of deformation of nanocrystalline materials. This task is made complicated by the fact that the constitutive response of a grain boundary, which is usually obtained by testing a bicrystal, accounts for both interface behavior (atom shuffling, sliding, GB dislocations) and grain bulk behavior (lattice dislocations, mechanical twinning). This investigation provides new insights into the influence of grain size on the mechanical properties of Σ tilt bicrystals in Cu and Al. Molecular static simulations incorporating the quasicontinuum theory were used to model the shear and separation of a bicrystal containing a boundary at its center. The grain size was varied from few atomic planes up to 100 nm. Both symmetric and asymmetric tilt grain boundaries were investigated. It is observed that the grain size has a strong effect on the maximum grain boundary strength, which is related to the nature of mechanisms triggered in the GB vicinity. Atom shuffling process is shown to have the most significant contribution in the decrease of boundary strength. This process is found related to the grain boundary structure through migration of GB defects.

Micromechanics of Advanced Materials II (Symposium in Honor of James C.M. Li's 80th Birthday): Dislocation Mechanics of Plasticity

Sponsored by: Structural Materials Division, ASM International: Materials Science Critical Technology Sector, SMD-Mechanical Behavior of Materials-(Jt. ASM-MSCTS)

Program Organizers: Fuqian Yang, University of Kentucky, Department of Chemical and Materials Engineering, Lexington, KY 40506 USA; C. C. Chau, Pactiv Corporation, Canandaigua Technology Center, Canandaigua, NY 14424 USA; Sung Nee George Chu, Multiplex Inc, South Plainfield, NJ 07080 USA; M. Ashraf Imam, Naval Research Laboratory, Materials Science & Technology Division, Washington, DC 20375-5343 USA; Teh-Ming Kung, Eastman Kodak Company, Rochester, NY 14650 USA; Peter K. Liaw, University of Tennessee, Materials Science and Engineering, Knoxville, TN 37996-2200 USA; B. B. Rath, Naval Research Laboratory, Materials Science and Component Technology Directorate, Washington, DC 20375-5341 USA

Monday AM Room: 3000
February 14, 2005 Location: Moscone West Convention Center

Session Chairs: F. R.N. Nabarro, University of the Witwatersrand, Sch. of Physics, Johannesburg S. Africa; M. A. Meyers, University of California, Matls. Sci. & Engrg., La Jolla, CA 92093 USA

8:30 AM Opening Remarks: Dr. William D. Nix

8:35 AM Invited
Chemical Theory of Dislocation Mobility: *John Joseph Gilman*[1]; [1]University of California, Matls. Sci. Dept., 6532 Boelter Hall, Los Angeles, CA 90095 USA

The conventional theory of dislocation mobility (Peierls-Nabarro theory) considers the geometry of dislocation cores, but not their chemistries. As a result it does not agree with the experimental facts. An adequate theory should take into account differing bonding types: covalent, metallic, ionic, or dispersion. Dislocation lines move when kinks along their lengths move. These kinks may be either sharp or diffuse depending on the bonding type. Diffuse kinks, as in simple metals, offer no resistance to kink motion, so electron and phonon viscosity determine mobility. At sharp kinks in covalent crystals, embedded chemical exchanges determine the mobility. Walsh correlation diagrams can be used to calculate mobilities in this case.

8:55 AM Invited
A Dislocation Multiplication Length Scale for Plasticity: Strain Hardening in Small Crystals by Dislocation Starvation: *William D. Nix*[1]; Julia R. Greer[1]; Gang Feng[1]; [1]Stanford University, Dept. Matls. Sci. & Engrg., 416 Escondido Mall, Stanford, CA 94305-2205 USA

For more than 50 years strain hardening of soft metal crystals has been understood as a process of dislocation multiplication and elastic interaction. According to this classical picture one might expect small crystals with free surfaces to be soft and to exhibit little strain hardening. Dislocations created by multiplication might be free to leave the crystal before interacting with other dislocations. But if dislocations multiply through the glide motion of other dislocations, as J.J. Gilman and others argued nearly forty years ago, then there is a length scale for the multiplication process, related to the average distance a dislocation glides before creating another. When the crystal size is less than this length scale, dislocations would leave the crystal faster than they are created by multiplication. As a consequence, the crystal would be expected to initially soften before hardening by a process of dislocation starvation. As the dislocation density approaches zero, nucleation of new dislocations either at free surfaces or within the bulk of the crystal would be required to maintain plastic flow. The flow stress needed for these processes would approach the theoretical strength of the crystal. We have recently conducted deformation experiments in crystals on a small scale to shed light on these processes. In particular, we have conducted uniaxial compression experiments on tiny samples of single crystal gold made by focused ion beam machining and integrated circuit fabrication methods. These experiments involve small deformation volumes and minimal strain gradients. They show that sub-micron sized crystals become remarkably stronger as they are plastically deformed and approach the theoretical strength after 10-20% strain. The results are consistent with picture of strain hardening by dislocation starvation, which is expected when the crystal size is less that the length scale for dislocation multiplication.

9:15 AM Invited
Length Scales for Volumes Small in 2 and 3 Dimensions: *William W. Gerberich*[1]; [1]University of Minnesota, Chem. Engrg. & Matls. Sci., Minneapolis, MN 55455-0132 USA

Mechanically, very thin films, nanospheres, nanotowers, nanoboxes and other small geometric features are principally characterized by nanoindentation. Such structures have the additional commonality of small volume (V) to surface area (S) associated with the required small indentation depth. Since it has been shown that V/S as a length scale can be related to both surface energy effects at small penetration and dislocation hardening at deeper depths, this is used as a predictor of flow strength. In terms of V/S there are several ways to define a length scale. One could take the entire volume and divide by the entire surface area or alternatively find the ratios of just the deformed volume to the contact surface area. If you assess the former, you find that a solid cube of height, h, or a solid sphere of diameter,d, gives a length scale of h/6 or d/6. This compares to a hollow cube or sphere with length scale of t/2 with t the wall thickness. This gives a reasonable representation of yield strength for the initial deformation using an Orowan criterion. Thus thin-walled structures may have length scales much smaller than their solid counterparts, the implication being that these would support higher load without permanent deformation. At larger strains where constraint is supplied by a diamond contact on the top and a hard substrate on the bottom, a linear hardening model based on dislocation spacing is more appropriate. This gives a length scale of 2b(h-Ä)/Ä where b is the burgers vector and Ä is displacement. One can also compare this to h/6 for a solid cube which implies a greater strength for a thin-walled box undergoing displacements of Ä > b/12. To first order these give predictions of the flow strength as a function of displacement. Results on titanium, silicon and aluminum will be presented. The impact of such length scales on both the analysis of constitutive relations for small volumes and the use of these in computational materials science is discussed.

9:35 AM
Correlating Changes in Dislocation Substructures to Plasticity Size-Effects in FCC-Derivative Metals: *S. J. Polasik*[1]; D. M. Dimiduk[2]; M. D. Uchic[2]; H. L. Fraser[1]; M. J. Mills[1]; [1]Ohio State University, Matls. Sci. & Engrg. Dept., 477 Watts Hall, 2041 College Rd., Columbus, OH 43210 USA; [2]Air Force Research Laboratory, Matls. & Mfg. Direct., AFRL/MLLM, 2230 10th St., Wright Patterson AFB, OH 45433 USA

Using current micromechanical fabrication and testing methods, it is now possible to systematically explore size effects related to mechanical properties, i.e., changes in mechanical response due simply to shrinking the physical size of the deforming volume. Interesting new size effects have been discovered in the uniaxial compression testing of micron-size single-crystal samples for both pure Ni and Ni_3Al alloys, where for the latter the flow stress has been observed to increase in proportion to the inverse-square-root of the sample diameter. The size effects in Ni are not as dramatic, but there is a distinct transition in mechanical properties as the sample size shrinks below 10 microns in diameter. However, to date there is still not a connection between these size effects and observable changes to the dislocation substructure, namely because of the challenges in preparing transmission electron microscope (TEM) foils from miniature test specimens. In this study, we present the results of TEM analysis of deformed microsamples in the aforementioned materials, in order to gain a better understanding of the effect that artificially truncating the sample volume has on the fundamental micromechanisms of dislocation glide, storage, and multiplication.

9:55 AM Invited
Grain Boundary Contributions to Deformation and Solid-State Flow in Severe Plastic Deformation: *Erika V. Esquivel*[1]; L. E. Murr[1]; [1]University of Texas, Metallurgl. & Matls. Engrg., 500 W. Univ. Ave., El Paso, TX 79968 USA

More than 40 years ago, Professor Jim Li put forth the concept of grain boundary ledges as sources for dislocations. Since then, there have been numerous confirmations of grain boundary dislocation sources, consistent with the fundamental features of interfaces, and we will demonstrate these observations in deformed metals and alloys observed in the TEM after specific levels of plastic strain. More recently, Professor Li has proposed a new mechanism for severe plastic deformation, or superplastic flow beyond the normal realm of plasticity which involves a so called "interfacial fluid" that allows for continuous, solid-state flow accommodating large plastic strains, and even very high strain rates. Some interesting examples of severe plastic

deformation illustrating these issues, and the connectedness to the incipient and normal plastic regime (the stress-stain diagram) will be presented by examining high velocity and hypervelocity impact craters in polycrystalline metals and alloys. These exhibit varying degr ees of plastic strain and associated microstructures evolving from dislocation emission and interaction, and the actual plastic flow and jetting of solid-state material from the crater rims, which are shown to be arrays of adiabatic shear bands composed of dynamically recrystallized grains. The concept of an "interfacial fluid" will be examined considering dense dislocation arrays in the grain boundary phase regime utilizing the amorphous dislocation lattice concept also originated by Professor Li several decades ago.

10:15 AM Break

10:20 AM Invited
Dislocation Pile-Ups: From {110} Cracking in MgO to Modern Theoretical Strength Considerations: *Ronald W. Armstrong*[1]; [1]University of Maryland, Mechl. Engrg., College Park, MD 20742 USA

Early researches of Professor J.C.M. Li and colleagues dealt with modeling a secondary role of mutually-blocked dislocation pile-ups in producing otherwise unexpected {110} cracks at diamond pyramid hardness indentations put into {001} MgO crystal surfaces. Continuing research has shown that the surface displacements at such indentations are uniquely tied to the primary dislocation motions. But it is the cumulative dislocation interactions in the pile-ups, say, as revealed in x-ray diffraction topographs, that establish the local build-up of stress concentrations magnifying the applied loading forces. In polycrystals, there are analogous grain boundary blockages of the egress of slip or twinning deformation system displacements leading to quantitative description of an inverse square root of grain diameter dependence of the applied stress for cleavage fracturing and, also, a similar dependence for the yield and plastic flow stress; that is, the so-called Hall-Petch (H-P) dependencies for these respective stresses. In this case, Li and Chou provided a classic paper assessing the theoretical role of dislocation pile-ups in the flow stress/grain size relationships, covering analytical and numerical evaluations of dislocation pile-up properties, whether modeled as the real discrete entities or in terms of continuous distributions of dislocations with infinitesimal dislocation Burgers vectors. The latter consideration is critical in establishing the essential equivalence of a dislocation pile-up and a shear crack, as described on a continuum mechanics basis. Thus, there is connection between the Griffith-Irwin-Orowan fracture mechanics (FM) description of precracked polycrystal properties and the H-P dependence, at least, for cleavage, or reasonably brittle, fracturing. Added complication occurs, therefore, when both FM and H-P dependencies are coupled in determining the fracturing properties of real materials. One beneficial consideration is that effective grain size refinement can be understood to provide both an increase in yield strength and greater fracture toughness of a polycrystalline material. Lastly, there is the rather direct consideration of how far one can go in strengthening a material by reducing its grain size. Here, Li and Liu have modeled the behavior of circular dislocation pile-ups involving small numbers of dislocations that transition, in the limit, to the stress requirement for one dislocation loop expanding against the grain boundary resistance. And, in this case, near theoretical limiting strength levels are predicted for crack-free polycrystals unless other grain boundary weakening mechanisms come into play.

10:40 AM Invited
Dislocation Density Model for the Effect of Grain Size on the Flow Stress of a Ti-15.2 at.% Mo β-Alloy at 4.2-650 K: *Hans Conrad*[1]; Kai Wang[1]; [1]North Carolina State University, Matls. Sci. & Engrg., Raleigh, NC 27695-7907 USA

The effect of grain size d (4.6-22 μm) on flow stress σ and dislocation density ρ of a Ti-15.2 at.% Mo β-alloy was determined at 4.2-650 K. The grain size dependence of the flow stress was given by the Hall-Petch equation. Moreover, the dislocation density increased with increase in strain and decrease in grain size. The effect of grain size on the flow stress in terms of the dislocation density was given by $\sigma=\sigma_0(T)+C\rho^{1/2}$ where C was relatively independent of strain, grain size and temperature. The results are discussed in terms of the mechanisms for the effects of grain size and temperature on the flow stress.

11:00 AM Invited
Boundary Strengthening in Undeformed and Deformed Polycrystals: *Niels Hansen*[1]; [1]Risoe National Laboratory, Matls. Rsch. Dept., Ctr. for Fundamental Rsch.: Metal Struct. in 4-D, Roskilde DK-4000 Denmark

The Hall-Petch relation between the stress and the grain size is discussed separately for the yield stress of undeformed polycrystalline metals and for the flow stress of deformed metals. In the former case the grain size is the key structural parameter whereas in the latter structural parameters characterizing the dislocation structure must also be taken into account. An analysis of experimental data supports the Hall-Petch relation for undeformd metals over a grain size range from about 20 nanometers to hundreds of micrometers. For deformed metals where the microstructure evolves with increasing strain the strength of boundaries is not a constant and the Hall-Petch relation must be modified. To rationalize the observed behaviour different mechanisms for strengthening by high angle boundaries and dislocation boundaries will be discussed.

11:20 AM Invited
Flow Processes in Superplastic Yttria Stabilized Zirconia - A Deformation Limit Diagram: *N. Balasubramanian*[1]; Terence G. Langdon[2]; [1]R V College of Engineering, All India Council of Techl. Educ., Mysore Rd., Bangalore 560 059 India; [2]University of Southern California, Aeros. & Mechl. Engrg. & Matls. Sci., Olin Hall of Engrg., Rm. 430G, 3650 McClintock Ave., Los Angeles, CA 90089-1453 USA

The possible rate controlling mechanisms in the deformation of superplastic 3Y-TZP are considered. Several attempts have shown that intragranular dislocations have limited role at stresses below 100 MPa at temperatures 1573 to 1873 K, as the stress is too low to generate them. A single rate controlling mechanism is proposed consistent with a single activation energy observed. This is the interface-reaction controlled grain boundary diffusion creep. An equation derived on the basis of the above mechanism fits the data obtained by different investigators on the stress dependence of strain rate within a factor of 10. A deformation limit diagram is constructed to show that different regions with specific combinations of stress and grain size exponents are limiting cases of one and the same mechanism discussed above.

11:40 AM Invited
Influence of Microstructures on Deformation Behavior of Silicon Single Crystals: *Subhash Mahajan*[1]; [1]Arizona State University, Cheml. & Matls. Engrg., PO Box 876006, Tempe, AZ 85287-6006 USA

We have investigated the deformation behavior of as-grown float zone (FZ) and Czochralski (CZ) silicon single crystals. The CZ crystals contain oxygen, and this is above the solubility limit. Thus, by annealing microstructures of CZ crystals can be modified by precipitating oxygen. The as-grown FZ and CZ crystals exhibit pronounced yield drops and Lüders bands at 700°C. The magnitude of the yield drop decreases as the deformation temperature increases. The yield drops seen in the CZ crystals at 700°C can also be eliminated by annealing them prior to testing. In addition, Lüders front has well defined crystallography and its propagation can be likened to stress-induced migration of small angle tilt boundaries. Arguments will be developed to rationalize these observations.

12:00 PM Invited
Extended Planar Dislocation Boundaries in Metals Subjected to Plane Strain Deformation: *Xiaoxu Huang*[1]; John A. Wert[1]; [1]Risoe National Laboratory, Matls. Rsch. Dept., Ctr. for Fundamental Rsch.: Metal Struct. in 4-D, Roskilde DK-4000 Denmark

During plastic deformation of single crystals, various kinds of deformation bands are developed due to the localization of deformation on different length scales. In the case of plane strain deformation, the concept of equivalent slip systems has been proposed to simplify the mechanical analysis of the macroscopic crystal rotation associated with the deformation banding. A physical manifestation of equivalent slip systems has been found in the coincidence between the equivalent slip plane and the planar dislocation boundary planes experimentally observed in single crystals with high-symmetry crystal orientation subjected to plan strain deformation. In this work similar mechanical analysis is made for warm rolled interstitial steel to understand the correlation between the extended planar dislocation boundary planes and the active slip systems.

12:20 PM
Plastic Deformation Mechanisms of Pure Metals at Low Homologous Temperatures: *Chen-Ming Kuo*[1]; [1]I-Shou University, Dept. of Mechl. Engrg., 1, Sect. 1, Hsueh-Cheng Rd., Ta-Hsu, Kaohsiung 84008 Taiwan

Plastic deformation mechanisms of pure metals at low homologous temperatures are attributed to the motion of dislocations and their interactions with each other or other kinds of obstacles. Physically based modeling of these mechanisms is generally considered as thermally activated motion of dislocations past obstacles and structural evolution of the obstacles. In this study, stress rate change experiments, which give rapid stress changes, are conducted using pure copper at room temperature. Incremental method is employed in the

numerical simulation of above modeling. Excellent agreement is observed in the comparison between experimental data and numerical calculations. Sensitivity analyses are also performed to better understand both flow kinetics and structural evolution law. Simple kinetic model such as the regular distributed rectangular obstacle is adequate enough. Obstacle structure is strongly influenced by the dislocation annihilation processes.

Microstructural Processes in Irradiated Materials: Modelling Defect Evolution

Sponsored by: Structural Materials Division, SMD-Nuclear Materials Committee-(Jt. ASM-MSCTS)
Program Organizers: Brian D. Wirth, University of California, Department of Nuclear Engineering, Berkeley, CA 94720-1730 USA; Charlotte S. Becquart, Ecole Nationale Superieure de Chimie de Lille, Laboratoire de Metallurgie Physique et Genie des Materiaux, Villeneuve d'Ascq cedex 59655 France; Hideki Matsui, Tohoku University, Institute for Materials Research Japan; Lance L. Snead, Oak Ridge National Laboratory, Metals and Ceramics Division, Oak Ridge, TN 37830-6138 USA

Monday AM Room: 3011
February 14, 2005 Location: Moscone West Convention Center

Session Chairs: Maria Jose Caturla, Universidad de Alicante, Fisica Aplicada, Alicante E-03690 Spain; Charlotte S. Becquart, Ecole Nationale Superieure de Chimie de Lille, LMPGM, Villeneuve d'Ascq Cedex 59700 France

8:30 AM Invited
Atomistic Modelling of Point Defects and Impurities in Steels: *Graeme J. Ackland*[1]; [1]University of Edinburgh, Sch. of Physics, 5411 JCMB, Kings Bldgs., Edinburgh, Scotland EH9 2LZ UK

Results are presented for computer simulations of the behaviour of defects and impurities in alpha-iron under irradiation. Ab initio simulations are used to provide data for parameterisation of new interactomic potentials for iron with dilute impurities of Cu, P, Al and C. Molecular dynamics calculation of point defects and their interaction with impurities are presented. From these we attempt to determine coarse-grained objects (defect-impurity clusters) suitable for use as the fundamental objects in defect-dynamics calculations (e.g. kinetic Monte Carlo, dislocation dynamics). The stability/mobility of these emergent objects is checked by subsequent ab initio calculation such that the molecular dynamics/ab initio step of multiscale modelling is done self-consistently.

9:10 AM
Multiscale Modeling of Defect Kinetics in Electron Irradiated Iron: *Chu Chun Fu*[1]; Jacque Dalla Torre[1]; Francois Willaime[1]; Jean-Louis Bocquet[1]; Alain Barbu[1]; [1]CEA/Saclay, SRMP, Gif sur Yvette 91191 France

Changes in microstructure of nuclear materials are governed by the kinetics of defects produced by irradiation. The population of vacancies, interstitials, and their clusters can however be followed only indirectly, e.g. by macroscopic resistivity measurements. The information on the mobility, recombination, clustering or dissociation of defects provided by such experiments is both extremely rich and difficult to interpret. By combining ab initio and kinetic Monte Carlo methods, we successfully reproduce the abrupt resistivity changes — so called recovery stages — observed upon annealing after electron irradiation in pure iron. New features in the mechanisms responsible for these stages are revealed. We show that small vacancy clusters and tri-interstitials contribute to the stages attributed to mono-vacancy and di-interstitial migration respectively, predict the effect of the unexpected low migration barriers found for tri- and quadri-vacancies. The influence of carbon atoms on the recovery stages are also discussed.

9:30 AM
Weak-Beam Imaging of Small Point-Defect Clusters Using the Howie-Basinski Equations and the Multi-Slice Method: Z. Zhou[1]; S. L. Dudarev[2]; *M. L. Jenkins*[1]; A. P. Sutton[1]; M. A. Kirk[3]; [1]University of Oxford, Dept. of Matls., Parks Rd., Oxford, Oxfordshire OX1 3PH UK; [2]EURATOM/UKAEA Fusion Association, Theory & Modlg. Dept., Culham Sci. Ctr., Oxfordshire OX14 3DB UK; [3]Argonne National Laboratory, Matls. Sci. Div., Argonne, IL 60439 USA

Nanometer-sized dislocation loops and other small point-defect clusters are commonly found in irradiated materials. Complete characterisation of such defects often is very difficult. They are usually investigated by using diffraction contrast images produced by conventional transmission electron microscopy (TEM), particularly under weak-beam conditions which offer improved contrast and resolution compared with other imaging conditions. Image simulations obtained under the same conditions are necessary for a full analysis of such images. Such simulations may be carried out by solving the equations of dynamical diffraction theory. In the present work we have employed the Howie-Basinski equations rather than the usual Howie-Whelan equations, since weak-beam images of very small clusters are better simulated without the use of the column approximation. In simulations of this kind it is usual to obtain the displacement fields or strain fields by elasticity theory. It is well known that this method has limitations in the core region of defects, due to the inaccuracy of elasticity theory in this region. This disadvantage of the Howie-Basinski approach can be overcome by using strain fields calculated from atomistic configurations of small defects. The atomistic structures were obtained by conjugate-gradient (CG) energy minimisation. Simulations were carried out for dislocation loops and for stacking-fault tetrahedra. Weak-beam images were calculated using the Howie-Basinski approach and the multi-slice method for the same atomic structures to compare the capabilities of the two methods in TEM weak-beam imaging. The advantages and disadvantages of the two approaches will be discussed and comparisons made with experimental images.

9:50 AM
Effect of the Interatomic Potentials on Point-Defect Clustered Fraction in Molecular Dynamics Displacement Cascades Simulated in bcc-Fe: *Dmitry A. Terentyev*[1]; Christina Lagerstedt[2]; Pär Olsson[3]; Kai Nordlund[4]; Janne Wallenius[2]; Lorenzo Malerba[1]; [1]SCK-CEN, RMO, Boeretang 200, Mol 2400 Belgium; [2]Royal Institute of Technology, Dept. of Nucl. & Reactor Physics, Roslagstullsbacken 21, Stockholm SE-106 91 Sweden; [3]Uppsala University, Dept. of Neutron Rsch., Ångstrom Lab., Box 525, Uppsala SE-751 20 Sweden; [4]University of Helsinki, Accelerator Lab., POB 43 (Pietari Kalmin katu 2), Helsinki 00014 Finland

Depending on the interatomic potential used for molecular dynamics simulation of displacement cascades in bcc-Fe, primary states of damage characterised by different spatial distributions of point-defects (average clustered fractions) are obtained. These differences may influence the long-term microstructural evolution predicted by, e.g., kinetic Monte Carlo codes. In this work, a number of displacement cascades initiated by recoils of 5, 10 and 20 keV have been simulated using four different interatomic potentials for á-Fe, each providing, among other things, different descriptions of self-interstitial behaviour in this metal. The corresponding defect clustered fractions (for both self-interstitial atoms and vacancies) have been studied using the same criteria for cluster definition and compared. The outcome is discussed in terms of how the point-defect description provided by the potential used may influence the predicted primary state of damage.

10:10 AM Break

10:40 AM Invited
Ab Initio Modeling of Defect Properties With Substitutional and Interstitial Elements in Steels and Zr Alloys: *Christophe Domain*[1]; [1]EDF R&D, MMC, Les Renardières, Moret sur Loing F-77250 France

In steels, the constituting elements interact with each other as well as with point defects. In Zr alloys, in addition to these interactions, hydrogen pick up modifies the mechanical properties. The microstructure properties are directly linked to the chemical interactions between the different constituting elements, and the point defects or the extended defects (stacking faults, dislocation). All these atomic scale interactions govern the elementary mechanisms ruling the kinetics of the system, and are thus among the key parameters needed to model the evolution of the microstructure under ageing or irradiation. Ab initio methods allow to determine important quantities such as defect formation, binding or migration energies. Data on interstitial point defects (C, N, P) in Fe and H in Zr as well as on substitutional transition metal elements (Cu, Ni, Mn, Si, Cr, ...) interaction in bcc Fe will be presented and discussed. When available comparison with experimental data will be made in order to check the resul ts and in fine to predict unknown quantities. The link between the obtained atomic quantities and the related consequences on the macroscopic properties will be discussed.

11:20 AM
Point Defect Dynamics in Irradiated bcc Metals: *Joerg Rottler*[1]; David J. Srolovitz[1]; Roberto Car[1]; [1]Princeton University, PRISM, 70 Prospect Ave., Princeton, NJ 08544 USA

The macroscopic mechanical properties of irradiated metals are intimately related to their microstructural features and their spatiotemporal evolution. We present a statistical model for the dynamics of point defects in bcc metals that is solved through kinetic Monte Carlo (kMC) and rate equations. Self-interstitial atoms and vacancies can be produced in abundance upon irradiation with energetic particles, but they subsequently anneal due to recombination and absorption at sinks such as dislocations and grain boundaries. The model reveals a sequence of kinetic regimes that lead to a final steady state. We also determine the size distribution of voids that form when vacancies aggregate into cluster. The model is then extended to include long ranged elastic interactions between point defects and dislocations, which have so far mostly been ignored in kMC simulations of microstructural evolution. We also consider metal alloys, where interstitial and vacancy transport must be described through effective diffusivities and correlation effects become important.

11:40 AM
Kinetic Monte Carlo Simulation of Irradiation Effects in bcc Fe-Cu Alloys: Experimental Validation: *Lorenzo Malerba*[1]; Christophe Domain[2]; Charlotte S. Becquart[3]; Abderrahim Almazouzi[1]; [1]SCK CEN Nuclear Research Centre, Reactor Matls. Rsch. Unit, Boeretang 200, Mol B-2400 Belgium; [2]EDF R&D, Dept. Materiaux et Mecanique des Composants, Les Renardieres, Moret sur Loing F-77250 France; [3]USTL, Lab. de Métallurgie Physique et Génie des Matériaux, UMR 8517, Bat C6, Villeneuve d'Ascq F-59655 France

Iron-copper alloys are model materials for reactor pressure vessel (RPV) steels and are typically used in modelling-oriented experiments to gain insight into the basic mechanisms of steel embrittlement via copper precipitation and matrix damage formation. In this work a selection of positron annihilation and atom probe irradiation experiments on low-concentration Fe-Cu alloys available from the literature, complemented by dedicated thermal annealing experiments on Fe-1%Cu, is used as a reference to test the validity of a mesoscopic kinetic Monte Carlo model. In this model, the binding energies of copper-vacancy complexes (CuVC), which are among the main parameters governing the nucleation and growth of copper precipitates, are described using laws obtained from a detailed study of a large number of CuVC. In addition, a state-of-the-art description of SIA and SIA cluster mobility in Fe is applied. The validity of the model is assessed and possible further improvements of the model are discussed, based on the feedback from the experimental validation.

Multicomponent Multiphase Diffusion Symposium in Honor of John E. Morral: Analysis of Interdiffusion Mircrostructures: Session I

Sponsored by: Materials Processing & Manufacturing Division, Structural Materials Division, EMPMD/SMD-Alloy Phases Committee, MPMD-Solidification Committee, ASM/MSCTS-Atomic Transport Committee

Program Organizers: Carelyn E. Campbell, National Institute of Standards and Technology, Metallurgy Division, Gaithersburg, MD 20899-8555 USA; Ursula R. Kattner, National Institute of Standards and Technology, Metallurgy Division, Gaithersburg, MD 20899-8555 USA; Afina Lupulescu, Rensselaer Polytechnic Institute, Materials Science & Engineering, Troy, NY 12180-3590 USA; Yongho Sohn, University of Central Florida, Advanced Materials Processing & Analysis Center and Mechanical, Materials and Aerospace Engineering, Orlando, FL 32816-2455 USA

Monday AM — Room: 3007
February 14, 2005 — Location: Moscone West Convention Center

Session Chairs: Carelyn E. Campbell, National Institute of Standards and Technology, Metall., Gaithersburg, MD 20899-8555 USA; Samuel M. Allen, Massachusetts Institute of Technology, Dept. of Matls. Sci. & Engrg., Cambridge, MA 02139-4307 USA

8:30 AM Opening Remarks

8:35 AM Keynote
Diffusion Paths and Interdiffusion Microstructures: Applications and Remaining Challenges: *J. E. Morral*[1]; [1]Ohio State University, Dept. of Matls. Sci. & Engrg., Columbus, OH 43210 USA

Interdiffusion can influence the properties and cost of products that experience high temperature during processing or service (e.g. coated turbine blades, solid oxide fuel cells, carburized sun gears, etc.). Accordingly the ability to predict interdiffusion microstructures can be a useful alloy design tool. Software such as DICTRA can predict interdiffusion microstructures via diffusion paths and phase diagrams. Although useful for certain applications, both DICTRA and the theory of diffusion paths have serious limitations. Software for the Phase Field Method (PFM) requires more computer time, but has fewer limitations and can predict microstructures directly. Also the PFM takes into account both precipitate morphology and diffusion in precipitates, which yields a more accurate result. However without adequate databases and a better understanding of interdiffusion fundamentals, the value of these programs to alloy design will be limited.

9:15 AM Invited
Canonical Phase Diagrams: *John W. Cahn*[1]; [1]National Institute of Standards and Technology, MSEL, 100 Bureau Dr., Gaithersburg, MD 20899-8555 USA

The molar free energy of a solution F and its various derivatives with respect to concentrations can be used instead of the concentrations as the axes of phase diagrams. Such axes were explored by John Morral, in his paper "On Characterizing Stability Limits for Ternary Systems" (Acta Metall, 1972, 20, 1061). He found that when phase diagrams are plotted with second derivatives of F as axes instead of with the usual temperature and concentration axes, all regular solutions phase diagrams are distorted into triangular pyramids on a universal canonical phase diagram, in which stability limits are depicted as a double cone. One cone marks the stability limit with respect to continuous ordering and the other cone the stability limit with respect to spinodal decomposition. A solution's regular solution interaction parameters determines placement of each triangular pyramid phase diagram with respect to the double cone. This talk will explore some other choices of thermodynamics functions as axes. Phase diagram plots using axes of chemical potentials instead of concentration, as suggested by Scatchard and Pelton, are useful. Using derivatives of F w.r. to order parameters as axes gives canonical phase diagrams and insight into complex ordering, such as for Cu-Au, involving first-order phase transitions and more than one ordered phase.

9:45 AM Invited
Application of Diffusion Path Analysis in Determination of Phase Formation and Phase Diagrams: *J.-C. Zhao*[1]; [1]GE Global Research, One Rsch. Cir., K1-MB239, Niskayuna, NY 12309 USA

This presentation will give several examples to illustrate the applicability of diffusion path analysis in determination of phase formation in multicomponent diffusion couples. Very often regular plots of composition vs distance are not the most useful ones in understanding the formation of phases. The composition against composition plots are far more informative, especially when coupled with calculated multicomponent isothermal sections. In the latter case, it is important to select right elements to plot against one another to give the most valuable information. The composition against composition plots are also extremely useful for determination of phase diagrams using diffusion couples and diffusion multiples. Examples will be given for several ternary systems where the diffusion path analysis is essential for correct interpretation of the phase equilibrium data.

10:15 AM Break

10:30 AM Invited
Observations and Analysis of Interdiffusion Phenomena in Selected Multicomponent Systems: *Mysore A. Dayananda*[1]; [1]Purdue University, Sch. of Matls. Engrg., 501 Northwestern Ave., W. Lafayette, IN 47907 USA

Interdiffusion in multicomponent systems is reviewed with emphasis on the determination of interdiffusion fluxes and assessment of diffusional interactions among the components. The phenomena of uphill diffusion, zero-flux planes, diffusional instability at interfaces and microstructural evolution are illustrated with single phase and multiphase diffusion couples investigated in selected multicomponent systems. Uncommon diffusion paths and diffusion structures experimentally observed for single phase and multiphase diffusion couples in Cu-based and Fe-based ternary systems and ternary aluminides and silicides are presented and discussed in the light of diffusion paths, variation of diffusion coefficients with composition and grain boundary contributions to diffusion. The determination of interdiffusion coefficients from individual multicomponent diffusion couples and the generation of their concentration profiles from the calculated interdiffusion coefficients are also illustrated with the MultiDiflux program currently being developed. The research is supported by the National Science Foundation.

11:00 AM
Assessment of Analytical Methods for the Determination of Composition-Dependent Interdiffusion Coefficients in Ternary

Alloys: *Narayana Garimella*[1]; Abby Puccio[1]; Yongho Sohn[1]; [1]University of Central Florida, AMPAC & MMAE, Box 162455, 4000 Central Florida Blvd., Orlando, FL 32816-2455 USA

Understanding of concentration profiles and/or interdiffusion fluxes that develop in a ternary diffusion couple during an isothermal anneal generally entails the determination of interdiffusion coefficients based on extended Fick's law based on Onsager's formalism. The description of ternary diffusion requires four concentration-dependent interdiffusion coefficients, two main and two cross-coefficients. Several techniques including those based on Boltzmann-Matano analysis, and average interdiffusion coeffficients are available to analyze concentration profiles for the determination of ternary interdiffusion coefficients. Governing principles on these analytical methods are presented with concentration profiles obtained from selected isothermal diffusion studies in the alpha-phase (fcc) of Cu-Ni-Zn system at 775°C. Ternary interdiffusion coefficients determined based on these techniques are compared and complimented for the assessment of diffusional behavior and interactions in the Cu-Ni-Zn system at 775°C.

11:25 AM Invited
Microstructural Evolution in Interdiffusion Zones and its Effect on Diffusion Paths: Kaisheng Wu[2]; John E. Morral[1]; *Yunzhi Wang*[1]; [1]Ohio State University, Matls. Sci. & Engrg., 2041 College Rd., Columbus, OH 43210 USA; [2]University of Wisconsin, Matls. Sci. & Engrg., 1509 Univ. Ave., Madison, WI 53706 USA

The phase field method is being used to study explicitly the microstructural evolution that occurs in interdiffusion zones and its effect on diffusion paths. In this presentation we will discuss simulation results obtained from single-phase/two-phase and two-phase/two-phase diffusion couples of Ni-Al-Cr alloys. Free energy and mobility data of the system were obtained from CALPHAD databases. The simulated microstructural features and kinetics of boundary migration were compared with experimental observations. Also, diffusion paths calculated from the phase field simulations were compared with analytical and DICTRA predictions. The Kirkendall effect, Gibbs-Thompson effect, and the effect of nucleation on microstructural evolution and diffusion path shape will be addressed. This work is supported by the National Science Foundation.

11:55 AM
Trans-Interface Diffusion-Controlled Coarsening: *A. J. Ardell*[1]; V. Ozolins[1]; [1]University of California, Dept. of Matls. Sci. & Engrg., Los Angeles, CA 90095-1595 USA

We present a model of coarsening controlled by diffusion through the coherent interface between an ordered precipitate and a disordered matrix. Since chemical diffusion in ordered phases is much slower than in disordered phases, the interface is a diffusion bottleneck. The new theory predicts the following: The average radius squared increases linearly with time; Solute is depleted linearly with the inverse square-root of time; A scaled particle size distribution (PSD) that is much broader than the PSD of the LSW theory; The coarsening rates are completely independent of volume fraction. Published data on the coarsening of γ' (Ni_3Al) precipitates agree quite well with the new theory, which also predicts that coarsening of disordered γ (Ni-Al solid solution) precipitates in a γ' matrix should obey traditional LSW kinetics and be strongly volume-fraction dependent, as observed experimentally. No other theory is consistent with the totality of these experimental results.

Neutron Diffraction Characterization of Mechanical Behavior: Facilities, Techniques, and Capabilities

Sponsored by: ASM International: Materials Science Critical Technology Sector, Structural Materials Division, SMD-Mechanical Behavior of Materials-(Jt. ASM-MSCTS)
Program Organizers: Hahn Choo, University of Tennessee, Department of Materials Science and Engineering, Knoxville, TN 37996 USA; Camden R. Hubbard, Oak Ridge National Laboratory, Metals and Ceramics Division, Oak Ridge, TN 37831 USA; Peter K. Liaw, University of Tennessee, Materials Science and Engineering, Knoxville, TN 37996-2200 USA; Xunli Wang, Oak Ridge National Laboratory, Spallation Neutron Source, Oak Ridge, TN 37831 USA

Monday AM Room: 3004
February 14, 2005 Location: Moscone West Convention Center

Session Chairs: Hahn Choo, University of Tennessee, Dept. of Matls. Sci. & Engrg., Knoxville, TN 37996-2200 USA; Peter K. Liaw, University of Tennessee, Dept. of Matls. Sci. & Engrg., Knoxville, TN 37996-2200 USA

8:30 AM Invited
An Overview of the Spallation Neutron Source: *Ian S. Anderson*[1]; [1]Oak Ridge National Laboratory, Spallation Neutron Source, PO Box 2008, Oak Ridge, TN 37831-6474 USA

The Spallation Neutron Source is an accelerator-based neutron source being built in Oak Ridge, Tennessee. When completed in 2006 SNS will provide the most intense pulsed neutron beams in the world for scientific research and industrial development. The SNS is being built by a partnership of six DOE laboratories, and like all DOE facilities will be operated as a user facility, open to scientists and engineers from universities, industry, and government laboratories in the United States and abroad. Three cryogenic and one ambient water moderator will serve up to 24 instruments, 16 of which have been approved and are in various stages of construction. All instruments at SNS have been designed to be best in class and will provide unprecedented opportunities to explore the structure and dynamics of novel materials.

8:50 AM Invited
Compression Loading and Neutron Diffraction at Cryogenic Temperatures: *Mark A.M. Bourke*[1]; Don W. Brown[1]; Hahn Choo[2]; Bjorn Clausen[1]; Veronica Livescu[1]; Thomas A. Sisneros[1]; Raj Vaidyanathan[3]; [1]Los Alamos National Laboratory, LANSCE-12, Los Alamos, NM 87545 USA; [2]University of Tennessee, Matls. Sci. & Engrg., Knoxville, TN 37996 USA; [3]University of Central Florida, AMPAC/MMAE, Orlando, FL 32816 USA

A recent addition to the SMARTS instrument at the Los Alamos Neutron Science Center is an in situ cryogenic deformation capability. The capability allows neutron diffraction spectra to be recorded under uniaxial compression. This complements existing high (up to 1800K) temperature loading capability and has opened new areas of study. Current measurements have been performed at 200K but measurements at 150K are planned before the TMS '05 meeting. The design and modifications to the SMARTS load frame will be described. Preliminary results on transformations in R phase NiTi, twinning in Zirconium and strain induced martensite in steel will be presented to illustrate the potential of the new capability.

9:10 AM
In Situ Measurement of Texture and Elastic Strains with HIPPO-CRATES: *Sven C. Vogel*[1]; Christian Hartig[2]; Heinrich Mecking[2]; [1]Los Alamos National Laboratory, LANSCE-12, MS H805, PO Box 1663, Los Alamos, NM 87545 USA; [2]Technische Universität Hamburg-Harburg, Werkstoffphysik & Werkstofftechnologie, Eißendorfer Straße 42, 21073 Hamburg Germany

Neutron diffraction has been used to determine the elastic strains and texture evolution during plastic deformation of two materials: A two phase, powder-metallurgically (PM) produced 33vol.%Fe-67vol.%Cu alloy, and the Magnesium alloy AZ31. These were the first experiments with the new load-frame CRATES for the neutron diffractometer HIPPO at LANSCE. The unique HIPPO-CRATES combination allows deformation studies in-situ by following both lattice strain and texture changes in 20 sample directions per sample orientation. Both materials were tested in uni-axial compression and tension loading cycles up to a maximum plastic strain of 6.4 % (Fe-Cu) and 2.1 % (Mg-AZ31). Several neutron time-of-flight diffraction patterns were collected during the deformation, yielding information from many crystal lattice planes simultaneously. In the case of the Fe-Cu alloy

results were obtained elucidating the stress distribution during the plastic co-deformation of two ductile phases with very different yield stresses. Yield stresses of ~100 MPa and ~400 MPa were measured for the pure PM produced copper and iron materials, respectively. The evolution of the elastic strains in Fe and Cu is compared with FEM calculations for both phases based on input parameters obtained from macroscopic stress-strain curves of the individual materials. The variation of elastic strains and texture in the Magnesium alloy gives clear evidence about the activation of tensile twins at an early stage of plastic deformation.

9:30 AM
In-Situ Deformation of Cu Mosaic Crystals by TOF Neutron Transmission: *Javier Roberto Santisteban*[1]; [1]Open University, Matls. Engrg., Walton Hall, Milton Keynes MK2 2UT UK

We introduce the basic features of the neutron transmission by mosaic crystals through demonstration experiments comprising in-situ loading tests on plastically deformed Cu crystals, originally used as neutron monochromators. We show that these experiments can be used to monitor the variation in orientation, mosaic spread and interplanar distances, that occur as a result of elastic or plastic deformation. Distinctive features of this technique are the ability to study many crystal reflections simultaneously, together with the possibility of 2D spatial resolution. In its present state, it is possible to study the spatial distribution of a specimen's deformation in-situ over an area of 25x25mm2 with 2mm spatial resolution. We report the anisotropic evolution of the mosaic spread of a crystal as a result of plastic deformation. We present the dependence of the mosaic spread on the macroscopic shear strain and applied stress, as well as its spatial variation across the specimen.

9:50 AM
The TOF Strain Scanner POLDI with Multiple Frame Overlap - Concept and Performance: Uwe Stuhr[1]; Mirco Grosse[1]; *Werner Wagner*[1]; [1]Paul-Scherrer-Institute, Spallation Neutron Source Div., Villigen PSI 5232 Switzerland

POLDI is a new neutron diffraction instrument at the Swiss continuous spallation neutron source SINQ at PSI, primarily dedicated to residual stress investigations. The instrument has realized a novel type of time-of-flight (TOF) diffractometer allowing multiple frame overlap. Besides for the benefit of higher intensity (as compared to a conventional single-pulse mode), this concept allows an independent tuning of intensity and resolution, an immense advantage for a flexible adjustment to dedicated experiments. The concept makes use of the mutual dependence of the neutron's arrival time at the detector and the related scattering angle to assign the neutrons to the originating pulse at the chopper. The principle concept of the instrument, some special components, and the performance in terms of intensity, resolution and flexibility for strain mapping and structure analysis will be presented.

10:10 AM Break

10:30 AM Invited
Industrial Application of Residual Strain Measurement by Neutron in Japan: *Yukio Morii*[1]; [1]Japan Atomic Energy Research Institute, Neutron Sci. Rsch. Ctr., Tokai, Ibaraki 319-1195 Japan

The instrumental specifications and performance of the neutron diffractometer for Residual Stress Analysis, RESA, installed at JRR-3 of JAERI will be briefly introduced. New method of residual stress analysis, which does not require measurements of stress-free lattice space d0(hkl), was proposed and applied to evaluate the residual stress distribution in a welded sample. Preliminary results of the analysis will be discussed. Number of industrial application of neutron residual strain measurement is increasing in Japan. A few of the recent measurements will be introduced. The status of constructions of Japan Proton Accelerator Research Complex, J-PARC, and a Pulsed neutron diffractometer for Residual Stress Analysis, RESA-P, is briefly reported, with the activities supported by the local government to promote industrial research using neutron beam.

10:50 AM Invited
Neutrons at Work for Industry: *Ronald B. Rogge*[1]; [1]National Research Council, Canada, Neutron Prog. for Matls. Rsch., Chalk River Labs., Bldg. 459, Chalk River, Ontario K0J 1J0 Canada

In general diffraction is a powerful technique for gaining an understanding of the behaviour of materials. When combined with the high penetration of neutrons one has access to a uniquely powerful and non-destructive probe. Other presentations in this session show, for example, that in-situ loading experiments have revealed much about deformation in materials. It is also true that neutrons provide an excellent tool for evaluating and verifying real industrial processes and/or fabrication routes. This presentation will focus on examples in which neutrons have been put to work for industry, simulating realistic conditions, contributing to failure analysis, verifying the effectiveness of a processing steps, and dealing with regulatory bodies.

11:10 AM Invited
Neutron Strain Scanning: Going Beyond Present Limitations: *T. Pirling*[1]; [1]Institut Laue-Langevin, Diffraction Grp., 6 rue Jules Horowitz, F-38042 Grenoble France

Neutron strain scanning is nowadays a well-established method for the nondestructive determination of residual stresses in "real" engineering components. A big advantage of neutron strain-scanning are the high penetration power and the 90 degrees measuring geometry which allows, in almost all types of samples, measurements in all orientations necessary to determine the strain tensor. ILL has undertaken developments to improve resolution and utility of strain scanning instrumentation. These ideas are now part of the new instrument SALSA (Strain Analyser for Large and Small Applications) on which first tests are foreseen for August 2004. The construction of the instrument is a collaboration with the University of Manchester and partially founded by the EPSRC. Many instruments use slit apertures for defining the gauge volume. They have high transmission, but the inconvenience that they have to be placed as close as possible to the gauge volume. Measurements in big samples therefore show low lateral resolution be cause the gauge size increases with distance from the gauge volume due to the unavoidable beam divergence. This effect increases when focusing monochromators are used. However double focussing bent crystal monochromators seems to be most efficient for monochromatic strain scanning instrumentation. They take advantage of the divergence of the incident neutron beam and focus it to the gauge volume dimensions, without reducing the angular resolution of the instrument thanks to phase space focusing. The concept at ILL is to use radial focusing collimators for the beam definition, which takes advantage of the beam divergence and at the same time defines a precise gauge volume. Compared to using a slit, the distance to the gauge volume is several times higher. This enables measurements in big components with good precision. Another positive effect of the collimators is the reduction of the surface effect, which leads to huge errors in near surface or interface measurements. Using the collimator set-up, precise meas urements within twenty to fifty micrometres to an interface are possible, as well as measurements on samples that are thinner than the dimension of the gauge volume. Another limiting factor of instrumentation can be the sample alignment and positioning. The various, often complicated shapes of samples need a sample stage that is adaptable to all the different requirements. ILL has, in further collaboration with INRIA (France) and the manufacturer OHE (Switzerland), developed a design for a Stewart Platform (or hexapod) as sample stage. It allows tilt, rotation, oscillation and translation of the sample and scans along any trajectory in space. Its load capacity is more than 500 kg and samples up to 1.4 m in length can be mounted. The positioning accuracy lies in the range of 10 micrometres. The paper presents high resolution measurements mostly on aerospace applications and a short presentation of the new instrument SALSA.

11:30 AM Invited
Positron Annihilation as an Addidional Source of Information About Plastic Deformation in Structural Materials: *Hans Georg Priesmeyer*[1]; [1]Kiel University, Lab. for Applied Neutron Physics, c/o GKSS Rsch. Ctr., Max-Planck-Str.1, Geesthacht D-21502 Germany

During strain measurements by neutron diffraction additional information is available through simultaneous gamma-ray spectroscopy. Neutron absorption is always a competing process to neutron scattering. It leads to the emission of high-energy prompt gamma radiation, which in turn produces positrons within the bulk of the specimen. The subsequent decay of these so called antiparticles and the resulting annihilation radiation are influenced by material properties like defects. The interaction of positrons with electrons has in recent years become a successful technique to measure the momenta of electrons in solids. These are influenced by crystalline defects, such as dislocations created by plastic deformation. Experimentally, this leads to an increase in the mosaic spread of the BRAGG reflections for elastically scattered neutrons as well as changes of the shape of the 511 keV line of the positron annihilation radiation. Suitable collimation can assure that the information gathered by neutron diffraction and from positron annihilation comes from the same gauge volume. Correlation between the width of the BRAGG reflections and the S-parameter (describing the shape of the annihilation line) as a function of the degree of plastic deformation has been established. Experimental work of simultaneous on-line investigation of the plastic deformation behaviour of copper and aluminium as model substances is performed at the FRG-I research

reactor at GKSS and will be reviewed. Work funded by DFG Pr 267/13-1 and GKSS Research Centre Geesthacht GmbH.

11:50 AM
Design and Performance of the Second Generation Neutron Residual Stress Mapping Facility (NRSF2) at ORNL: *Camden Richards Hubbard*[1]; Alexandru D. Stoica[1]; Michael C. Wright[1]; Hahn Choo[1]; Stewart Craig[1]; William Bailey[1]; Fei Tang[1]; Ke An[1]; [1]Oak Ridge National Laboratory, Metals & Ceram. Div., MS 6064, Bldg. 4515, Oak Ridge, TN 37831-6064 USA

The NRSF2 design aims to improve the prior system's capabilities. Upgrades include utilizing: (a) the larger beam at HB-2; (b) two multiwafer Si, doubly focusing monochromators (wavelengths from 0.145 nm to 0.227 nm); (c) two high precision goniometers, one is capable of supporting large specimen mapping while the other enables strain tensor studies; and (d) and seven 40 x 100 mm active area 1-D position sensitive detectors. The flux on specimen is predicted to be close to 10**8 neutrons/cm**2/sec. The combined gains indicate approximately a 10-fold improvement in capability. A new load frame for tension/compression studies in the elastic, plastic and failure regimes of most materials has been developed. Environmental cells for use with the load frame for studies of environmental assisted corrosion studies using neutron strain mapping are also available. Results of monochromator, calibration, precision and performance will be reported.

Phase Stability, Phase Transformation and Reactive Phase Formation in Electronic Materials IV: Magnetic and Semiconducting Materials

Sponsored by: Electronic, Magnetic & Photonic Materials Division, Structural Materials Division, EMPMD/SMD-Alloy Phases Committee

Program Organizers: Douglas J. Swenson, Michigan Technological University, Department of Materials Science & Engineering, Houghton, MI 49931 USA; Srinivas Chada, Jabil Circuit, Inc., FAR Lab/Advanced Manufacturing Technology, St. Petersburg, FL 33716 USA; Sinn-Wen Chen, National Tsing-Hua University, Department of Chemical Engineering, Hsinchu 300 Taiwan; C. Robert Kao, National Central University, Department of Chemical and Materials Engineering, Chungli City 32054 Taiwan; Hyuck Mo Lee, Korea Advanced Institute of Science & Technology, Department of Materials Science & Engineering, Taejon 305-701 Korea; Suzanne E. Mohney, Pennsylvania State University, Department of Materials Science & Engineering, University Park, PA 16802 USA; Katsuaki Suganuma, Osaka University, Department of Nanomaterials and Environmental Conscious Technology, Ibaraki, Osaka 567-0047 Japan

Monday AM — Room: 3016
February 14, 2005 — Location: Moscone West Convention Center

Session Chairs: Douglas J. Swenson, Michigan Technological University, Dept. of Matl. Sci. & Engrg., Houghton, MI 49931 USA; Hyuck Mo Lee, Korea Advanced Institute of Science and Technology, Dept. of Matl. Sci. & Engrg., Taejon 305-701 S. Korea

8:30 AM Invited
Selective Oxidation of Tunnel Barrier Metals in Magnetic Tunnel Junctions: *Y. Austin Chang*[1]; [1]University of Wisconsin, Matls. Sci. & Engrg., 1509 Univ. Ave., Madison, WI 53706 USA

Oxidation of an ultra-thin metal layer (less than 1 nm) to form a quality oxide tunnel barrier is of critical importance in fabricating Magnetic Tunnel Junctions (MTJs) with low product of resistance and area (RA). The ultimate goal in this research is to utilize a scheme to completely oxidize the metal to form its oxide without oxidizing the adjacent ferromagnetic layers in such junctions. Indeed it is extremely difficult if not impossible to achieve this objective using the conventional plasma or air oxidation methods. However, it is possible to use a gas mixture with fixed chemical potential of oxygen in such way that only the tunnel barrier metal is oxidized but not the ferromagnetic layers. In this presentation, I will show experimental results obtained by these students in my group at the University of Wisconsin at Madison in oxidizing metals such as Al, Y etc. These results show that indeed the thin metal layers are completely oxidized but not the adjacent ferromagnetic layers such as CoFe.

9:00 AM Invited
In Situ Ultrahigh Vacuum Transmission Electron Microscope Investigations of Dynamical Changes of Nanostructures on Silicon: *L. J. Chen*[1]; [1]National Tsing Hua University, Matls. Sci. & Engrg., 101, sec. 2, Kuang Fu Rd., Hsinchu 300 Taiwan

In situ ultrahigh vacuum transmission electron microscope is a powerful tool to investigate the dynamic changes of nanostructures on silicon. By observing growth and phase transitions in situ, understanding of their mechanisms can be used to model relevant processes. With the precise knowledge of the changes occurred on an atomic level, accurate control of the growth process can be achieved. The dynamical changes occurred on the nano scale are often unexpected, which also underscores the importance of the approach. In this presentation, we will highlight several examples to demonstrate the unique capability of in situ TEM to study the dynamical changes. The examples include the formation and disintegration of TiSi2 nanowires in Ti/Si system, stacking and vibration of NiSi2 nanodots on silicon, migration of Au "block" on Si bi-crystal and epitaxial growth of beta-FeSi2 on silicon.

9:30 AM
Characterization of the Pd/GaSb Thin Film Reaction for Pd-Based Metallizations to GaSb: Suzanne Mohney[1]; *Joshua Alexander Robinson*[1]; [1]Pennsylvania State University, Dept. of Matls. Sci. & Engrg. & Matls. Rsch. Inst., 101 Steidle Bldg., Univ. Park, PA 16802 USA

GaSb plays a vital role in thermophotovoltaic, microwave, and optoelectronic devices. Knowledge based on the interaction of a metal and semiconductor, both in the bulk and thin film regime, is often used to engineer contacts to compound semiconductors. To date, information about the behavior of a Pd thin film on GaSb has been limited. In this study, we explore the interaction between a 50 nm layer of Pd and GaSb substrate annealed in the temperature range 100 - 350°C for 10 - 360 min. We report on the formation of Pd-rich nanocrystalline and polycrystalline ternary phases at temperatures below 200°C, followed by Pd-Ga and Pd-Sb binary phases above 300°C. Finally, we describe the development of low resistance ohmic contacts to n-GaSb using Pd as one of the contact metals.

9:50 AM
Self-Assembled Si-Ge Nanostructures on Si(100) and Si(110): *Douglas J. Swenson*[1]; Xurui Deng[1]; [1]Michigan Technological University, Dept. of Matls. Sci. & Engrg., 1400 Townsend Dr., Houghton, MI 49931 USA

Self-assembled, Group IV (Si, Ge, C, Sn) nanostructures exhibit an array of unique electronic and optoelectronic properties. The microstructural evolution of these structures results from the interplay of thermodynamic factors (bulk, interfacial and strain energy) and kinetic factors (e.g., surface diffusivities, material deposition rate). Here, the similarities and differences of microstructural evolution are presented for Si_xGe_{1-x} films grown under similar conditions by molecular beam epitaxy (MBE) on (100) and (110)-oriented Si substrates. In both cases, it is possible to create self-organized pits, decorated by islands of various shapes, under certain growth conditions. However, 2-D film growth is much more persistent on (110) surfaces than it is on (100) surfaces, and upon exceeding a critical film thickness, Si_xGe_{1-x} nanowires, aligned with the single in-plane <110> azimuth are observed. Rationale for these differences in morphology are given primarily in terms of strain energy and surface energy phenomena.

10:10 AM Break

10:30 AM Invited
The Application of the Solid State Electrochemical Method to the Investigation of Electronic Materials: *Krzysztof Fitzner*[1]; [1]AGH University of Science and Technology, Lab. of Physl. Chmst. & Electrochmst., Faculty of Non-Ferrous Metals, 30 Mickiewicza Ave., 30-059 Krakow Poland

Systematic electromotive force (emf) studies were carried out to determine thermodynamic properties of several semiconducting, magneto-optic and superconducting phases. First, electrochemical cells were used in coulometric titration experiments to determine the first order interaction parameters in the liquid III-V-O systems: In-As-O, Ga-As-O, In-P-O and Ga-P-O systems. Second, the stability of rare-earth manganates ($LnMnO_3$, where Ln = Nd, Pr, Sm, Gd, Ho and Yb) was determined using cells with a zirconia solid electrolyte. Finally, by combining the cells with zirconia and CaF_2 electrolytes, Gibbs energy changes of respective reactions of formation of $LnBa_2Cu_3O_7$ and Ln_2BaCuO_5 (where Ln = Yb, Tm, Er, Ho, Dy, Gd) were measured. New thermodynamic data are presented and discussed.

11:00 AM
A Thermodynamic Database for III-N Semiconductors: *Ursula R. Kattner*[1]; Albert V. Davydov[1]; Benjamin P. Burton[2]; [1]National Institute of Standards and Technology, Metall. Div., 100 Bureau Dr., Stop 8555, Gaithersburg, MD 20899-8555 USA; [2]National Institute of Standards and Technology, Ceram. Div., 100 Bureau Dr., Stop 8520, Gaithersburg, MD 20899-8520 USA

GaN and related nitrides are important materials for photonic and microelectronic devices. Development of optimum growth and thermal processing conditions for the device structures still relies mostly on trial-and-error methods. Knowledge of the thermodynamics of Group III-V systems is not only important for optimizing semiconductor growth/processing conditions but also key for understanding reactions with metal contact materials. Although binary phase diagrams of III-V materials appear to be simple with only one compound at 1:1 stoichiometry, development of thermodynamic descriptions is plagued by a lack of data and large uncertainties in the available data. Available thermochemical and phase diagram experimental data and ab-initio data will be discussed for some constituent binary and ternary systems, and a preliminary thermodynamic database will be presented. This database can be used to define growth and processing conditions of III-N compounds and for description of semiconductor-metal contacts.

11:20 AM
Designing Experimental Determination of Sheet Resistance of a Submicron Titanium Self-Aligned Silicide Formation: *Jau Shiung Fang*[1]; Chen Siang Hsu[1]; [1]National Huwei University of Science and Technology, Dept. of Matls. Sci. & Engrg., 64 Wunhua Rd., Huwei 632, Yunlin 632 Taiwan

The sheet resistance of titanium self-aligned silicide was shown to determine the optimum process of a 0.25 mm polysilicon gate technology. The influence of arsenic doping dosage, the thickness of titanium, the temperature of rapid thermal annealing on the sheet resistance of a polysilicon gate was experimentally analyzed. Experimental results revealed that thickness of titanium, the temperature of RTP-2, and the interaction between the thickness of titanium and the temperature of RTP-2 dominated the sheet resistance of TiSi2. Statistical analysis showed that sheet resistance decreased as titanium thickness increased or RTP-1 temperature increased. An optimum RTP-2 temperature was also required for reducing sheet resistance of TiSi2. A low sheet resistance was yielded for titanium thickness = 32-35 nm, RTP-1 = 720-750°C for 75 sec, and RTP-2 = 860°C for 20 sec.

Phase Transformations Within Small-Size Systems: Thermodynamics, Phase Equilibria and Kinetics

Sponsored by: Materials Processing & Manufacturing Division, MPMD-Phase Transformation Committee-(Jt. ASM-MSCTS), EMPMD/SMD-Chemistry & Physics of Materials Committee, EMPMD-Nanomaterials Committee
Program Organizers: Vijay K. Vasudevan, University of Cincinnati, Department of Chemical and Materials Engineering, Cincinnati, OH 45221-0012 USA; Robert D. Shull, National Institute of Standards and Testing, Metallurgy Division, Gaithersburg, MD 20899-8552 USA; George Spanos, Naval Research Laboratory, Physical Metallurgy Branch, Washington, DC 20375-5000 USA; Xinghang Zhang, Texas A&M University, Department of Mechanical Engineering, College Station, TX 77843-3123 USA

Monday AM Room: 3002
February 14, 2005 Location: Moscone West Convention Center

Session Chairs: George Spanos, Naval Research Laboratory, Washington, DC 20375-5000 USA; Robert D. Shull, National Institute of Standards and Testing, Metall. Div., Gaithersburg, MD 20899-8552 USA

8:30 AM Opening Remarks: Vijay Vasudevan, George Spanos, Robert Shull and Xinghang Zhang

8:40 AM Invited
Two-Phase Equilibrium in Individual Nanoparticles of Bi-Sn: *William A. Jesser*[1]; C. Thomas Schamp[1]; [1]University of Virginia, Matls. Sci. & Engrg., 116 Engrs. Way, PO Box 400745, Charlottesville, VA 22904-0745 USA

When evaluating the path of phase transformations in systems with nanoscopic dimensions one often relies on bulk phase diagrams for guidance because of the lack of phase diagrams that show the effect of size. In order to provide insight into how the phase diagrams vary when a high surface curvature exists, binary alloys of Bi and Sn were prepared as a collection of individual crystalline particles vapor deposited onto amorphous carbon substrates in ultra-high vacuum. These crystallites were annealed after deposition to equilibrate the phases and structures. After annealing they were transferred to the transmission electron microscope for analysis of the phase state as a function of composition and surface curvature, i.e., particle radius. Individual crystallites were analyzed with respect to crystallinity, two-phase or one phase coexistence, and composition. The data show that there is a critical size below which there is no limit to the solubility, in strong contrast to that found in the bulk system, which is a simple eutectic alloy with only a few percent solubility on the bismuth-rich solid solution side of the phase diagram and about 15% on the tin-rich side. The change in solubility limit with size was found to be very strong in the bismuth-rich terminal solid solution and very-weak in the tin-rich terminal solid solution. A thermodynamic approach to using free-energy expressions modified to account for surface curvature can be successful in showing the shift in solubility with size. It is shown that the appropriate thermodynamic potential to minimize is a modified Helmholtz free energy.

9:15 AM Invited
In Situ TEM Observation of Alloy Phase Formation in Isolated Nanometer-Sized Particles: *Hirotaro Mori*[1]; JungGoo Lee[1]; [1]Osaka University, Rsch. Ctr. for Ultra High Voltage Electron Microscopy, Yamadaoka 2-1, Suita, Osaka 565-0871 Japan

Alloy phase formation in nanometer-sized particles has been studied by in-situ TEM using particles in the Au-Sn, Bi-Sn, and Pb-Sn systems. It is revealed that not only the surface energy but also the interface energy of an interface between two different phases (solid-solid or solid-liquid) significantly changes the phase equilibrium of nanometer-sized particles. For example, due to the interface energy of an interface between two different solid phases, the eutectic point in the three alloy systems decreases much faster than the melting point in pure substance with decreasing size of particles. Furthermore, it is revealed that the solid solubility is greatly enhanced in nanometer-sized alloy particles. In approximately 16-nm-sized lead solid solution, the tin solubility was higher than 56 atomic percent at 110 degrees, which is almost five times higher than that in the corresponding bulk material. Factors governing the phase equilibrium of nanometer-sized alloy particles will be discussed.

9:50 AM Invited
Interface-Controlled Phase Equilibria in Nanoscale Systems: *Gerhard Wilde*[1]; [1]Research Center Karlsruhe, Inst. of Nanotech., PO Box 3640, Karlsruhe D-76021 Germany

Phase equilibria in nanoscale systems, e.g. of matrix-embedded nanoparticles, can deviate strongly from the phase diagrams valid for the respective macroscopic system. Specifically, the observation of size-dependent melting transformations has stimulated controversial discussions concerning the underlying mechanism. Yet, recent experimental results indicate that the shift of the melting temperature at small system size is thermodynamic in nature, as opposed to explanations based on nucleation kinetics, and that the topology of the particle/matrix interface controls the phase transformation. In multicomponent and nanoscaled alloy systems, interface segregation and interface-induced stresses are known to affect the phase boundary lines of the phase diagrams. Yet, already the presence of internal heterophase interfaces contributing an excess free energy is sufficient to severely modify the phase equilibrium and the associated phase transformations in nano-size alloy systems. Here, new results on the constitutive behavior of binary nanoscaled model alloys, obtained by experiment and calculation, will be highlighted.

10:25 AM Break

10:40 AM Invited
Structural and Compositional Transformations in Nanocrystals: *Paul Alivisatos*[1]; [1]University of California, Dept. of Chmst, D-43A Hildebrand Hall, Berkeley, CA 94720 USA

The kinetics of structural and compositional transformations in nanocrystals is markedly different and more homogeneous than in bulk solids. This talk will review several such changes including pressure induced isomerizations, cation exchanges, and reactions involving interdiffusion.

11:15 AM Invited
Surface-Stress Effects on the Phase Equilibrium in Nanoscale Metal Hydrides: *Jörg Weissmüller*[1]; Christian Lemier[1]; [1]Forschungszentrum Karlsruhe, Inst. of Nanotech., PO Box 3640, Karlsuhe D-76021 Germany

Size-dependent shifts in the chemical equilibrium can arise from elastic interaction between interfaces and the bulk, e.g. in solid solutions equilibrated with a reservoir of solute at controlled chemical potential. Changes in the local composition give rise to forces at surfaces, which must be balanced by stress in the bulk. The pressure can reach values of several GPa; it affects the chemical potential as well as the apparent solute-solute interaction energy. Metal hydrides provide model systems for related experimental studies, since hydrogen can be ex-changed reversibly. By combining the analysis of the simultaneous chemical and mechanical equilibrium with experimental data for nanoscale metal hydrogen systems, one can measure the interface stress as a function of the chemical potential, and one can measure the 'stretch', a deformation normal to the interface. At nanometer system size, the equilibrium phase diagrams of solid solutions with a miscibility gap are strongly affected by elastic interactions.

Precious Metals: Au, Ag, Pt, Pd, Os, Rh, Ir, Ru

Sponsored by: Extraction & Processing Division, Light Metals Division, EPD-Aqueous Processing Committee, EPD-Precious Metals Committee, EPD-Pyrometallurgy Committee, LMD/EPD-Recycling Committee
Program Organizer: Richard S. Kunter, Behre Dolbear Company, Golden, CO 80401-9420 USA

Monday AM Room: 2022
February 14, 2005 Location: Moscone West Convention Center

Session Chair: Richard S. Kuech, Behre Dolbear Company, Golden, CO 80401-9420 USA

8:30 AM
Effect of Magnetic Field on the Permeation of Hydrogen in Ni-Pd Alloys: *Sivaraman Guruswamy*[1]; Purushottam Kumar[1]; Robert Pennington Corson[1]; Pinai Mungsantisuk[1]; Michael L. Free[1]; [1]University of Utah, Metallurgl. Engrg., 135 S. 1460 E., Rm. 412, Salt Lake City, UT 84112-0114 USA

This paper examines the effect of magnetic field on the diffusivity of hydrogen isotopes in Ni-Pd alloys. Ni-Pd is an interesting alloy system for this study since both Ni and Pd absorb hydrogen, NiPd alloys shows significant magnetostrictive strain, and Ni-Pd system exists as a continuous single-phase region over the entire composition range. Electropermeation method as devised by Devanathan and Stachurski was used in this study. In this method, the coverage of hydrogen on one side of the NiPd alloy membrane is maintained at a constant level by cathodically charging hydrogen while it is anodically maintained at zero level on the other (discharge)side. The current on the discharge cell circuit gives the permeation rate. Alloys examined include Ni-70 at.% Pd alloy that shows a large magnetostrictive strain. Diffusivity of hydrogen calculated using lag times shows significant changes under a magnetic field. Support by University of Utah gratefully acknowledged.

8:55 AM
Magnetostriction and Magnetic Properties of PdX (X=Fe, Ni, Co) Single Crystals: *Purushottam Kumar*[1]; Robert Pennington Corson[1]; Pinai Mungsantisuk[1]; Sivaraman Guruswamy[1]; [1]University of Utah, Metallurgl. Engrg., 135 S. 1460 E., Rm. 412, Salt Lake City, UT 84112-0114 USA

Fe-Pd, Co-Pd, and Ni-Pd alloy systems show appreciable magnetostrictive strains that are of interest for sensor applications. These systems exhibit congruent melting minima. In this work, we have examined the magnetic and magnetostrictive behavior of congruent melting Fe-Pd, Co-Pd, and Ni-Pd compositions. The alloys examined include Fe- 54.9 at.% Pd, Ni-45 at.% Pd, and Co-45 at.% Pd. The paper describes the growth of bulk single crystals of these alloys using Czochralski technique. X-ray diffractometer was used to obtain rocking curves that were used to determine the [001] crystal direction. Magnetostriction in [001] direction was measured using strain gages. Magnetic properties were measured using a vibrating sample magnetometer. NiPd showed the highest magnetostriction values among the congruent melting compositions. Magnetic and Magnetostrictive behavior of these alloy single crystals are presented. Work partially supported by NSF Grant # DMR 0241603.

9:20 AM
Magnetostriction and Magnetic Properties of Polycrystalline PdX (X=Ni, Co, Fe) Alloys: *Pinai Mungsantisuk*[1]; Kevin Nguyen[1]; Robert Pennington Corson[1]; Purushottam Kumar[1]; *Sivaraman Guruswamy*[1]; [1]University of Utah, Metallurgl. Engrg., 135 S. 1460 E., Rm. 412, Salt Lake City, UT 84112-0114 USA

The presence of congruent melting minima, the occurrence of ferromagnetic transition over a large composition range, and FCC type crystal structure make the Pd-Ni, Pd-Co, and Pd-Fe based systems attractive candidates in our search for materials with no rare-earths, large low-field magnetostriction, and good mechanical properties. The presence of paramagnetic-ferromagnetic transition over a broad range of composition also provides opportunity for fundamental studies. In this work, we have examined the microstructure, hardness, elastic modulus, magnetic and magnetostrictive behavior of Pd-Ni, Pd-Co, and Pd-Fe alloys over the entire composition range. Alloy sample rods were prepared by arc melting and casting. X-ray diffractometer was used to obtain lattice parameter and texture data. Magnetostriction was measured along the rod axis using strain gages. Magnetic properties were measured using a vibrating sample magnetometer. Elastic modulus measurements were made using RUS technique. Work supported by University of Utah and NSF-DMR Grant #0241603.

9:45 AM
An Electrochemical Investigation on Intensification of Gold Cyanidation by Heavy Metal Ions: *Guanghui Li*[1]; Yongbin Yang[1]; Qian Li[1]; Yufeng Guo[1]; Huang Zhucheng[1]; Tao Jiang[1]; [1]Central South University, Sch. of Resources Procg. & Bioengrg., Changsha 410083 China

The effects of heavy metal ions on gold cyanidation have been studied by using electrochemical techniques. Results show that addition of thallium, bismuth, silver, mercury and lead ions greatly widen potential zone of activation dissolution of gold and significantly improve the anodic current density. The suitable concentration of heavy metal ions for the activation is found to be 10-6M for lead, 10-5M for bismuth, 5×10-5M for mercury and 8×10-5M for silver. Gold dissolution rate increases continuously with thallium concentration within the range of 10-6-10-4M. Based on research results on anodic and cathodic processes, mixed-potential models of gold dissolution in the presence of heavy metal ions have been constructed. Investigation shows that the enhancing effect of the heavy metal ions on gold leaching is clearly improved if there are cathodic assistants such as hydrogen peroxide.

10:10 AM
Controlling Mercury Emissions with Spent Catalytic Converter Cores: *Zhiyong Xu*[1]; Jinjing Luo[1]; Robert Greenlund[1]; Bowen Li[1]; Jim Hwang[1]; [1]Michigan Technological University, Inst. of Matls. Procg., 1400 Townsend Dr., Houghton, MI 49931 USA

In this study the spent automobile catalytic converter cores were examined to evaluate the effectiveness of using treated spent automobile catalytic converter core materials as low cost, viable sorbents in the capture of mercury chemical forms associated with coal-fired power plant emissions. This study was conducted by comparing the mercury adsorption effect between spent catalytic converter core materials and activated carbons, common used mercury sorbents. The results showed that spent catalytic converter cores were significantly more effective than activated carbon.

Shape Casting — The John Campbell Symposium: Liquid Metal Quality

Sponsored by: Light Metals Division, LMD-Aluminum Committee, MPMD-Solidification Committee
Program Organizers: Murat Tiryakioglu, Robert Morris University, Moon Township, PA 15108 USA; Paul N. Crepeau, General Motors Corporation, MC/486-710-251, Pontiac, MI 48340-2920 USA

Monday AM Room: 2008
February 14, 2005 Location: Moscone West Convention Center

Session Chair: Diran Apelian, MPI - WPI, Matls. Sci. & Engrg., Worcester, MA 01609 USA

8:30 AM **Welcome:** Murat Tiryakioglu and Paul N. Crepeau

8:40 AM
Bifilms - The Most Exciting Discovery of the Century: *John Campbell*[1]; [1]University of Birmingham, Metall. & Matls., Elms Rd., N. Campus, Edgbaston, Birmingham, W. Midlands B15 2TT UK

A short overview is presented of the key role that bifilms play in the initiation of porosity, hot tears, and the control of ductility of cast metals. In addition, their transient nature in cast irons is indicated by

the recent studies of carbon films lining bubble trails, constituting leakage defects in grey iron castings. The role of bifilms in the control of cast structures in Al alloys appears extensive: (i) grain size is influenced by convection that can be suppressed by sufficiently large or numerous bifilms; (ii) DAS is sometimes controlled if the local region of the casting is separated from the bulk by bifilms, and undercools, giving a fine local DAS; and (iii) the mechanism of the modification of Al-Si alloys by Na and Sr is explained for the first time by the deactivation of bifilms as substrates for Si. It seems likely that the majority of all metal failures (whether of cast or wrought material) may be attributable to bifilms. Bifilms appear to be an important feature that we need to add to our metallurgical knowledge.

9:10 AM
A Method to Study the Life-Cycle of a Double Oxide Film Defect in Liquid Aluminum Alloys: *Ramin Raeiszadeh*[1]; W. D. Griffiths[1]; [1]University of Birmingham, Interdisciplinary Rsch. Ctr. in Matls. Procg., Dept. of Metall. & Matls. Sci., Elms Rd., Edgbaston, Birmingham, W. Midlands B15 2TT UK

Entrained double oxide films have been held responsible for a reduction in mechanical properties in aluminum casting alloys. However, to date, their life cycle in the liquid metal has not been studied directly. A silicon nitride rod with a 13.3 mm diameter hole in one end was plunged into liquid aluminum to hold a known volume of air in contact with the liquid metal at a controlled temperature. The change in the air volume with time was recorded by real time x-ray radiography to determine the reaction rates of the bubble atmosphere with the liquid aluminum as a model for the behaviour of an entrained double oxide film defect. The results showed that first oxygen and then nitrogen were consumed by the aluminum alloy to form aluminum oxide and aluminum nitride. The effect of adding different elements to the aluminum and different hydrogen contents has also been studied.

9:35 AM
The Use of Bifilm Index as an Assessment of Liquid Metal Quality: *Derya Dispinar*[1]; John Campbell[1]; [1]University of Birmingham, Metall. Matls., Elms Rd., N. Campus, Edgbaston, Birmingham, W. Midlands B15 2TT UK

There is growing evidence that, in general, aluminium castings under-perform by a large margin. This is not only because of shrinkage or gas porosity, but particularly because of existence of extremely thin but detrimental defects called bifilms. Bifilms are the initiators of porosity. The opening of a bifilm to make a pore involves negligible energy, being so easy that it can be assumed that this process will be overwhelmingly favoured. The discriminating use of the Reduced Pressure Test clearly reveals the existence of bifilms. Until now the unpredictable behaviour of bifilms has made the RPT hard to quantify. A new fundamental parameter is proposed here to assess melt quality called the Bifilm Index. Typical total bifilm lengths vary from 3 to 300 mm. The effect of the bifilm index on the mechanical properties was studied using several common Al-Si alloys cast under different conditions.

10:00 AM Break

10:10 AM
Preventive Metal Treatment Through Advanced Melting: *C. Edward Eckert*[1]; [1]Apogee Technology, 1600 Hulton Rd., Verona, PA 15147 USA

Conventional aluminum melting results in a deterioration of metal quality due to in-situ melt oxidation, exposure of molten metal to products of combustion, and from separation of the oxide envelope that surrounds the charge media. Peak melt surface temperatures in reverberatory melting can exceed 2000OF. This results in an increase in oxidation rate by a factor of 64, compared to a bulk temperature of 1350OF. Additionally, the dew point of typical products of combustion is equivalent to saturated air at 75OF, further exacerbating oxidation and establishing a high partial pressure of monatomic hydrogen. Such melting processes depend on downstream remedial metal treatment for removal of consequential inclusions and dissolved hydrogen. An advanced melting process has been developed under the support of the US Department of Energy Office of Industrial Technology, with the original objectives of minimizing specific melting energy and melts loss. This has been accomplished. In addition, it has been found that dissolved hydrogen levels well under 0.2 cm3 H2/100g Al, with a freedom from visible supernatant oxides, typify aluminum melted by this process. Importantly, the peak temperature attained is approximately 40OF lower than bulk temperature, and no products of combustion are produced. The melting process also includes an integral flotation device to separate surface oxides introduced by the charge media. Metal treatment has now become implicitly preventative through the use of advanced melting. This paper will describe the development, performance, and impact on metal quality that characterizes the advanced melting process. Preventative metal treatment represents a paradigm shift in aluminum melt preparation methodology.

10:35 AM
The Relation Between Al_3Ti Particle Formation and Impurity Removal During In-Situ Precipitation Treatment of Al-Ti-X Alloys: *Sompong Srimanosaowapak*[1]; Keyna O'Reilly[1]; [1]University of Oxford, Dept. of Matls., Parks Rd., Oxford OX1 3PH UK

Precipitation-sedimentation of Al_3Ti particles has been found recently by the authors[1] to increase the cleanliness of an Al-Ti melt. However, so far, little has been presented regarding quantitative evaluation of impurity removal by using this precipitation technique. In order to improve the understanding of the incorporation of impurities in precipitating particles in molten alloys, doping with different alloying elements and controlling the cooling rate during particle precipitation in Al-0.4, 0.6%Ti have been studied. Results indicated that elements, which have trialuminide structure, substantially substituted in the Ti sublattice of Al_3Ti. The reduction of impurity removal of solid inclusions by in-situ Al_3Ti precipitation with increasing cooling rate has been discussed by relating to the possibility of the reduction in incorporation by engulfment caused by relatively low Al_3Ti particle growth rates and the increase in convective flow within the melt at high cooling rates. [1]Srimanosaowapak, S. and O'Reilly, K.A.Q., Light Metals (Metaux Legers), 2004, 283-297.

11:00 AM
Panel Discussion: Inclusions in Aluminum Melting, Treatment and Casting: *David Neff*[1]; Paul N. Crepeau[2]; [1]Metaullics Systems, Solon, OH 44139 USA; [2]General Motors, 895 Joslyn Rd., MC 483-710-251, Pontiac, MI 48340 USA

A panel of 4 well-known figures in the aluminum casting industry will discuss a series of slides illustrating inclusions encountered in aluminum melting, treating and casting. This presentation is sponsored by the American Foundry Society and is an update of material shown at the most recent AFS Casting Congress. The material is will not be included in the conference transactions.

Superalloys and Coatings for High Temperature Applications: Bond-Coat Technologies - I

Sponsored by: Structural Materials Division, SMD-High Temperature Alloys Committee, SMD-Corrosion and Environmental Effects Committee-(Jt. ASM-MSCTS), High Temperature Materials Committee of IoM3

Program Organizers: Roger C. Reed, University of British Columbia, Department of Metals and Materials Engineering, Vancouver, British Columbia V6T 1Z4 Canada; Richard S. Bellows, Solar Turbines, Inc., Materials and Process Engineering, San Diego, CA 92186-5376 USA; Qiang (Charles) Feng, University of Michigan, Department of Materials Science and Engineering, Ann Arbor, MI 48109 USA; Tim Gabb, NASA Glenn Research Center, Cleveland, OH 44135 USA; John Nicholls, Cranfield University, Bedfordshire MK43 OAL UK; Bruce A. Pint, Oak Ridge National Laboratory, Oak Ridge, TN 37831 USA

Monday AM Room: Nob Hill A/B
February 14, 2005 Location: San Francisco Marriott

Session Chairs: Roger C. Reed, University of British Columbia, Dept. of Metals & Matls. Engrg., Vancouver, BC V6T 1Z4 Canada; Bruce A. Pint, Oak Ridge National Laboratory, Oak Ridge, TN 37831 USA

8:30 AM Invited
Environmental and Thermal Barrier Coatings for Gas Turbine Engine Components: Status and Challenges Ahead: *Ramgopal Darolia*[1]; [1]GE Transportation, Matls. & Process Engrg., 1 Neumann Way, MD M-89, Cincinnati, OH 45215 USA

The nickel-base superalloys used for high-pressure turbine (HPT) airfoils are subjected to very high temperatures, stresses and oxidizing and corrosive environments. Significant progress has been made in developing high strength superalloys as well as in advanced protective coatings. To reduce surface temperatures and durability of the airfoils, thermal barrier coatings (TBC) have been used for the past decade. An understanding of the behavior of two essential components of TBC (zirconia topcoat and the alumina forming bond coat) is essential for reliable utilization of TBC. The bond coat use temperature limits the maximum allowable TBC surface temperature partly due to potential for erosion and impact damage of TBC. Higher temperature bond

coats, and improvement in erosion and impact resistance of the topcoat are two key development needs. Coating/superalloy interactions are also concerns in higher refractory containing superalloys. As the TBC surface temperature is increased, phase and microstructural stability are other limiting considerations.

9:00 AM Invited
The Influence of Bond Coat Properties and Phase Transformations in the Degradation of Thermal Barrier Coatings: *Kevin J. Hemker*[1]; [1]Johns Hopkins University, Dept. of Mechl. Engrg., Baltimore, MD 21218 USA

Thermal barrier coatings (TBCs) used in gas turbine engines are comprised of multilayers with multiple functions. A ceramic top coat is the insulator, the formation of a thermally grown oxide (TGO) slows oxidation, the intermetallic bond coat provides a reservoir for TGO formation and improved adherence, and the superalloy substrate carries the loads. During thermal cycling, the interaction of these chemically and mechanically diverse layers determines the lifetime of the coating. The occurrence of a martensitic transformation in platinum modified nickel aluminide bond coats has been shown to promote TGO rumpling, which results in topcoat spallation. The interplay between transformation temperatures and elevated temperature creep strength of the bond coat holds particular importance, and both of these quantities have been shown to be extremely sensitive to alloy composition. This presentation will outline recent efforts to characterize the effect of alloying on the martensitic transformation temperatures of NiAl-based alloys and to measure the creep strength of various bond coat compositions with elevated temperature microsample tensile testing.

9:30 AM
Ru-Modified Platinum Aluminide Bond Coatings for TBC Systems: *Brian Tryon*[1]; Ken S. Murphy[2]; Carlos G. Levi[3]; Jingyu Yang[3]; Tresa M. Pollock[1]; [1]University of Michigan, Dept. of Matls. Sci. & Engrg., 3062 H. H. Dow Bldg., 2300 Hayward St., Ann Arbor, MI 48109 USA; [2]Howmet Research Corporation, 1500 S. Warner St., Whitehall, MI 49461 USA; [3]University of California, Matls. Dept., Santa Barbara, CA 93106 USA

Diffusional processes for the fabrication of multi-layered Ru-modified bond coats for thermal barrier coatings (TBCs) have recently been of interest for potentially prolonging the useful life of TBC systems. Ru-modifications have been made to a conventional Pt-modified nickel aluminide diffusion bond coating for thermal barrier coating systems. Interdiffusion and phase equilibria issues involved in the fabrication of the coating have been investigated. Structure evolution at various stages of the coating process has been studied with scanning electron microscopy and electron microprobe analysis. A comparison between the oxidation characteristics of the Ru-modified Pt-aluminide coating and conventional Pt-aluminide coatings is presented.

10:00 AM
Oxidation Behavior of RuAl Intermetallics: Paul Bellina[1]; Amalia Catanoiu[1]; Francisco M. Morales[1]; *Manfred Rühle*[1]; [1]MPI für Metallforschung, Heisenbergstr. 3, Stuttgart 70569 Germany

Bond coats (BC) play a crucial role in the performance of thermal barrier coatings (TBC) systems. Ru alloys and Ru-containing intermetallics were identified as promising candidates. Systematic studies were performed on the oxidation behavior of near stoichiometric â-RuAl alloys. Thermal gravimetric analyses (TGA) were performed in oxygen or air at 1100°C for different times ranging from 0.1 h to 500 h. Microstructural studies were performed by SEM and TEM. Results of the oxidation showed a á-Al2O3 layer lying on top of a ä-Ru layer. Specific microstructural instabilities can lead to a sequence of alternating á-Al2O3/ä-Ru layers or to the formation of large elongated cavities parallel to the surface. Selected area diffraction (SAD) and high-angle annular dark field (HAADF) studies of the interfaces were performed. The results and implications will be discussed on the basis of an oxidation model. Work supported jointly by the NSF (DMR-0099695) and the EC (G5RD-CT2000-00573).

10:30 AM Break

10:50 AM
Analyses of Failure Mechanisms and Microstructural Characterization of a Thermal Barrier System with a Two-Phase Bond Coat Based on NiCoCrAlY: *Christopher Mercer*[1]; Sabine Faulhaber[1]; Tau Xu[1]; Anthony G. Evans[1]; [1]University of California, Matls. Dept., Engrg. II, Rm. 1355, Santa Barbara, CA 93110 USA

The mechanisms of failure of an EB-PVD thermal barrier coating (TBC) with a NiCoCrAlY bond coat have been ascertained on test specimens subjected to thermal cycling in a burner rig. In regions where the TBC is still intact, the morphology and microstructure of the thermally-grown oxide (TGO) has been characterized using a combination of scanning and transmission electron microscopy. Compositional analysis was carried out in the TEM using an energy-dispersive spectroscopy system with element mapping capabilities. In addition, sub-surface features were explored using a focused ion beam instrument with imaging capabilities. The TGO was found to exhibit a very non-uniform morphology and a complex microstructure and composition. A dominant delamination has been identified extending primarily along the interface between the TGO and the bond coat, but traversing the TGO at imperfections (pegs) leaving TGO islands embedded in the bond coat. Analytical modeling has revealed that the principal stresses induced around the pegs and energy release rates for interface cracks remain invariant on a cycle-by-cycle basis, and are too small to nucleate an interface crack. The implication is that occasional large imperfections nucleate interface delaminations. Once formed, these delaminations become unstable and propagate along the interface.

11:15 AM
Oxidation Resistance of Ir-Pt Coated Ni-Base Superalloys Prepared by Electorodeposition Method: *Aya Suzuki*[1]; Yingna Wu[2]; Yoshinobu Yamamoto[3]; Hideyuki Murakami[4]; [1]National Institute for Materials Science, High Temp. Matls. Grp., Matl. Engrg. Lab., 1-2-1 Sengen, Tsukuba Sci. City, Ibaraki 305-0047 Japan; [2]National Institute for Materials Science, Thermal Spray Grp., Matl.. Engrg. Lab., 1-2-1 Sengen, Tsukuba Sci. City, Ibaraki 305-0047 Japan; [3]National Institute for Materials Science, Non-Oxide Ceram. Grp., Advd. Matl. Lab., 1-1 Namiki, Tsukuba Sci. City, Ibaraki 305-0044 Japan; [4]University of Tokyo, Dept. of Matls. Engrg., Sch. of Engrg., 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656 Japan

Pt-modified aluminide coatings, as well as MCrAlY overlay coatings have widely been used as bond coat materials for thermal barrier coating systems. Recent investigation also proposed that Pt coated and simply annealed samples demonstrated better oxidation resistance than simply aluminized specimens. In this study, we propose electrodeposited Ir-Pt coatings because Ir may play a role as a solid-solution hardener of Pt-base coatings with maintaining oxidation resistance. The effects of composition and post electrodeposition treatment, on the characteristics of the coated materials were investigated. aim of this study is to investigate the high-temperature characteristics of Ir-Pt alloy coatings prepared by the electrodeposition process. Ir-Pt alloys with various compositions were coated on Ni-base sigle crystal superalloy TMS-82+ substrates. They were then treated by the conventional Al-pack-cementation process (typically 1273K for 5h). Cyclic oxidation tests, hot-corrosion tests and high-temperature mechanical test were conducted to characterize the high-temperature mechanical properties.

11:40 AM
A Platinum-Enriched γ+γ' Bond Coat with Different Hf Contents: *Y. Zhang*[1]; B. A. Pint[2]; J. A. Haynes[2]; L. D. Chitwood[2]; [1]Tennessee Technological University, Dept. of Mechl. Engrg., 115 W. 10th St., Box 5014, Cookeville, TN 38505-0001 USA; [2]Oak Ridge National Laboratory, Metals & Ceram. Div., Oak Ridge, TN 37831-6156 USA

The constant demand for increased operating temperatures in gas turbine engines has been the driving force for development of more reliable thermal barrier coating (TBC) systems. Recently, it has been recognized that compared to the commercial single-phase β-(Ni,Pt)Al bond coat, a two-phase γ+γ' coating could offer some potential advantages such as higher creep strength, better compatibility between coating and superalloy substrate, improved metallurgical stability, and reduced manufacturing cost. In this study, a Pt-enriched γ+γ'-type coating has been applied to a directionally-solidified René 142 superalloy with three different Hf contents (0.02, 0.76, and 1.37 wt.%). The γ+γ' coating was prepared by electroplating a thin layer of Pt (~7μm) on the superalloy substrate followed by a diffusion treatment in vacuum at 1150°C. Isothermal and cyclic oxidation tests were conducted on the coated specimens at 1100 and 1150°C. It was found that the oxidation performance of the γ+γ' coating was comparable to the β-(Ni,Pt)Al coating and much better than the simple β-NiAl coating at the same testing temperature. The beneficial effect of Hf was clearly demonstrated by the fact that the oxidation behavior of the γ+γ' coating was proportional to the Hf content of the substrate, with higher Hf levels resulting in improved performance.

12:05 PM
Degradation of Protective Coatings Under Thermal and Mechanical Loading: *Bernd Baufeld*[1]; Marion Bartsch[1]; Serdar Dalkiliç[2]; Michael Heinzelmann[3]; [1]German Aerospace Center, Inst. of Matls. Rsch., Porz-Wahnheide, Linder Höhe, Köln, Nordrhein-Westfalen 51147 Germany; [2]Anadolu University, Coll. of Civil Aviation, Eskisehir 26470 Turkey; [3]Fachhochschule Bonn-Rhein-Sieg, Technische

Mechanik & Festigkeitslehre, Von-Liebig-Straße 20, Rheinbach, Nordrhein-Westfalen 53359 Germany

Different high temperature testing schemes like cyclic thermal, cyclic mechanical at constant high temperatures, and cyclic thermal mechanical, the latter either with or without additional temperature gradient, were performed on specimens with a NiCoCrAlY coating and in some cases with an additional thermal barrier coating (TBC). While the testing under thermal mechanical loading with thermal gradient is the most complex, it simulates most closely in-service conditions for internally cooled components. The resultant defects and the degradation evolution proved to depend critically on the testing scheme and on the presence of the TBC. With the help of finite element analysis the observed defects can be related with the testing condition. The results suggest the possibility to deduce the prevailing conditions from the observed defects. Furthermore, they show the necessity to design laboratory tests as realistic as possible, especially if the test data are used for lifetime assessment.

Texture and Microstructure in Thin Films and Coatings: Copper Metallization

Sponsored by: ASM International: Materials Science Critical Technology Sector, ASM/MSCTS-Texture & Anisotropy Committee
Program Organizers: David P. Field, Washington State University, Pullman, WA 99164-2920 USA; Chris A. Michaluk, Williams Advanced Materials, Gilbertsville, PA 19525 USA; John E. Sanchez, Advanced Micro Devices, Sunnyvale, CA 94088 USA; J. A. Szpunar, McGill University, Department of Metallurgical Engineering, Montreal, Quebec H3A 2A7 Canada

Monday AM Room: 3010
February 14, 2005 Location: Moscone West Convention Center

Session Chairs: John E. Sanchez, Unity Semiconductor, Sunnyvale, CA USA; Kris Kozaczek, Hypernex Inc., State College, PA 16801 USA

8:30 AM Invited
Texture-Related Reliability Problems of Cu Thin Films For Semicondutor Application: *Junichi Koike*[1]; Makoto Wada[1]; [1]Tohoku University, Dept. of Matls. Sci., 02 Aoba, Aramaki, Aoba-ku, Sendai, Miyagi 980-8579 Japan

Cu thin films have been extensively studied in the past decade for interconnect application in advanced semiconductor devices. Texture and microstructure of the Cu film have been known to influence the interconnect reliability. The presentation will address three important topics for the reliability of the Cu thin films with regard to the dependence of initial film texture on (1) room-temperature self-annealing, (2) the texture after heat treatment and (3) the formation of voids under thermal stress conditions. The observed results can be consistently explained by considering a large elastic anisotropy of Cu, elastic energy density and stress distribution.

9:00 AM
Textures of Copper Interconnects with Different Geometries: *Dong-Nyung Lee*[1]; Hyo-Jong Lee[1]; Ui-Hyung Lee[1]; Sook-Hoon Kang[1]; Kyu-Hwan Oh[1]; [1]Seoul National University, Rsch. Inst. of Advd. Matls. & Sch. of Matls. Sci. & Engrg., Seoul Korea

The properties of deposited metal films and interconnect structures at submicrometer scale are sensitive functions of microstructural features. Therefore, understanding of the factors which control microstructural evolution is necessary for the development and design of reliable, manufacturable interconnect structures, especially in copper damascene interconnects. In this study, the trench width of copper interconnects was increased from 0.2 to 6 microns at a given space of 0.2 microns and the space was increased from 0.2 microns to 1 microns at a given width of 0.5 microns. The interconnects were annealed in various ways, UV heating at 200°C immediately after electrodeposition, UV heating at 200°C after self-annealing for 3 h, and self-annealing for a week. The annealed interconnects were subjected to the texture-measurement by EBSD. The texture changed from {111}<110> to {111}<112> and eventually to <111> fiber with increasing trench width, and tended to change from {111}<112> to {111}<110> with increasing space regardless annealing conditions. The results were discussed based on the strain-energy-release-maximization, in which the annealing texture is determined such that the minimum Young's modulus direction of annealed grains is parallel to the maximum stress direction of deposits.

9:20 AM
Investigating the Texture and Grain Boundary Character of ECD Copper Films Using Orientation Imaging: *Matthew Nowell*[1]; Aaron Frank[2]; [1]TSL/EDAX, 392 E. 12300 S., Ste. H, Draper, UT 84020 USA; [2]Texas Instruments, TX USA

The use of copper as a device interconnection material in integrated circuit devices has developed through the use of the damascene manufacturing process due to the need to improve electromigration failure resistance. In this process the copper metal is electrochemically deposited onto the oxide substrate and fills patterned interconnect trenches. Chemical-Mechanical polishing (CMP) then removes the overburden film, and leaves only the copper interconnections. The diffusion barrier layers between the oxide and the deposited film and the current densities used in the deposition process can influence the texture and grain boundary character of the resulting copper film. Additionally, the thermal annealing prior to CMP will also affect the microstructure. In this work, orientation imaging microscopy (OIM) is used to investigate the effects of barrier layer material and deposition current density on texture and grain boundary development during copper deposition. The effects of subsequent thermal annealing are also addressed.

9:40 AM
Texture Evolution During Annealing of Electroplated Cu Films: *Nojin Park*[1]; David P. Field[2]; Matthew M. Nowell[3]; [1]Kumoh National Institute of Technology, Sch. of Advd. Matls. & Sys. Engrg., 188 Shin Pyung Dong, Kumi, Kyung Buk 730-701 Korea; [2]Washington State University, Mechl. & Matls. Engrg., Box 642920, Pullman, WA 99164-2920 USA; [3]TexSEM Laboratories/EDAX, 392E 12300S, Ste. H, Draper, UT 84020 USA

Structural evolution during annealing of electroplated copper films is a strong function of film processing parameters, including sublayer material and thickness, bath chemistry, film thickness, and annealing temperature, among others. Because electroplating of copper into narrow trench structures is employed in the fabrication of modern integrated circuits, understanding structural evolution becomes important in controlling properties and maintaining uniformity of the circuit. A {111} fiber texture is generally assumed to be the preferred structure in such films. The strength of this texture weakens dramatically by the accumulation of twin boundaries that are prevalent in relatively low stacking fault metals such as copper. Evolution of both texture and grain boundary structure are examined by use of in-situ investigations using electron backscatter diffraction.

10:00 AM Break

10:30 AM
Role of Substrate in Influencing High Temperature Behavior of Cu Film Studied In-Situ by EBSD: *Kabirkumar Mirpuri*[1]; Jerzy A. Szpunar[1]; [1]McGill University, Matls. Engrg., M. H. Wong Bldg., 3610 Univ. St., Montreal, QC H3A 2B2 Canada

High temperature behavior of Cu films is studied in-situ in SEM by electron back-scatter diffraction (EBSD). The microstructure of the films was already stabilized. Two different investigations were performed at RT, 200 and 400°C. The film showed the presence of (111) fiber texture together with {111}<110> and {111}<112> preferred orientations. In the first investigation the strength of {111}<110> became stronger compared to {111}<112> while in second it became weaker. Similar investigation for freestanding Cu film did not show any such texture transformation making it clear that substrate had a role to play. To ascertain the mechanism by which substrate was influencing texture transformation, the average misorientation between the neighboring scan points was computed in the range of 2 to 7°. The (111) grains with lower values of misorientation were termed as recrystallized and were supposed to be showing lower dislocation activity. The grains with larger values of misorientations were termed as substructured and were suppose to be showing higher dislocation activity. It was found that in the first investigation where the {111}<110> component became relatively stronger at higher temperature the increase in the percentage of substructured {111}<110> grains was lower compared to the second investigation where the increase in the percentage of the substructured {111}<110> grains was higher compared to first investigation. Interestingly, the {111}<110> component became relatively weaker during the second investigation with increasing temperature. Thus, clearly it seems that the dislocations have a role in deciding the strength of {111}<110> component. The inclination of the {111}<110> and {111}<112> grains to the specimen surface was computed as a function of temperature for both the investigations. The tilt of these grains as a means of stress relaxation in relation to dislocation activity is discussed. The information gained from these experiments could be used to explain similar texture transformation in

the Cu damascene lines where we observed a stronger tendency of the system to have preferred {111}<112> orientations for the larger linewidths in the as-deposited condition for the cases where the lines were closely spaced.

10:50 AM
Effects of Surface Condition and Clean Techniques on Cu Films for the Quality of Cu Wafer Bonding: *K. N. Chen*[1]; C. S. Tan[1]; A. Fan[1]; R. Reif[1]; [1]Massachusetts Institute of Technology, Microsys. Tech. Labs., 60 Vassar St., Rm. 39-623, Cambridge, MA 02139 USA

In order to achieve Cu wafer bonding with good quality, surface conditions of Cu films are important factors. In this work, the effects of surface conditions such as surface roughness and oxide formation on the bonding strength are investigated under different bonding conditions. Some Cu wafers were cleaned using HCl before bonding in order to remove the surface oxide. Surface roughness of Cu film with and without HCl clean was examined. Since surface clean before bonding removes oxides but creates surface roughness, it is important to study the corresponding bonding strength under different bonding conditions. These results offer the required information for the process design of Cu wafer bonding.

11:10 AM
Microstructure Cu-Cr Coatings: *Kuang-Tsan Kenneth Chiang*[1]; Ronghua Wei[1]; James Arps[2]; Vijay Jain[1]; [1]CNWRA-SwRI, CSPE, 6220 Culebra Rd., San Antonio, TX 78238 USA; [2]SwRI, 6220 Culebra Rd., San Antonio, TX 78238 USA

Copper alloys and composites are of interest for high strength and high thermal conductivity applications at elevated temperatures. However, their usage at high temperatures is usually limited by severe oxidation attack. In this investigation, Cu-Cr coatings with Cr contents of 10-50 weight percent were produced by vacuum-based ion beam deposition techniques. The coating microstructure was characterized by scanning electron microscopy, x-ray diffraction, and transmission electron microscopy. Oxidation kinetics of the coatings was evaluated using a continuous-recording microbalance. At low Cr contents, the oxidation rates were controlled by outward diffusion of copper ions to form external Cu-oxides. For high Cr contents, a fine-grained Cr-rich oxide was formed on the coating surface. The effect of coating microstructure on high temperature oxidation resistance will be discussed.

11:30 AM
Effect of Low-K Dielectric on Textural and Microstructural Evolution of Cu Damascene Interconnects: *Jae-Young Cho*[1]; Jerzy A. Szpunar[1]; [1]McGill University, Metals & Matls. Engrg., 3610 Univ. St., Montreal, Quebec H3A 2B2 Canada

As the features of integrated circuitry (IC) chips are scaled to deep submicron dimensions, the signal delay (the resistance-capacitance delay) caused by interconnect becomes a dominant factor limiting speed performance. To reduce this delay, it is recommended to replace Al by Cu and to introduce low-k dielectric. From the previous research, it was found that the distribution of stress can be a major factor affecting textural and microstructural evolution of Cu damascene interconnects in embedded the SiO2 dielectric during annealing. Since the low-k material has significantly higher thermal expansion coefficient (CTE) than Cu and SiO2, it can generate very different thermal stress distribution in the trench during annealing. In addition, the pitch width can affect the stress distribution during annealing. To analyze a relationship between the stress distribution and textural evolution in the samples investigated, changes of the micro stress were calculated from the different pitch width using FEM in both SiO2 and low-k dielectric materials. It was found that the inhomogeneity of stress distribution in Cu interconnects is an important factor required for understanding textural evolution after annealing. Textural evolution in damascene interconnects lines after annealing was analyzed depending on dielectric materials used and the pitch width.

The Armen G. Khachaturyan Symposium on Phase Transformation and Microstructural Evolution in Crystalline Solids: Session I

Sponsored by: Electronic, Magnetic & Photonic Materials Division, Materials Processing & Manufacturing Division, EMPMD/SMD-Chemistry & Physics of Materials Committee, MPMD-Computational Materials Science & Engineering-(Jt. ASM-MSCTS), MPMD-Phase Transformations Committee-(Jt. ASM-MSCTS)
Program Organizers: Yunzhi Wang, Ohio State University, Department of Materials Science and Engineering, Columbus, OH 43210 USA; Long-Qing Chen, Pennsylvania State University, Materials Science and Engineering Department, University Park, PA 16802-5005 USA; John William Morris, University of California, Department of Materials Science and Engineering, Berkeley, CA 94720 USA

Monday AM — Room: 3003
February 14, 2005 — Location: Moscone West Convention Center

Session Chairs: John William Morris, University of California, MSE, Berkeley, CA 94720 USA; Yunzhi Wang, Ohio State University, MSE, Columbus, OH 43210 USA

8:30 AM Opening Remarks

8:35 AM Keynote
Multi-Scale Theory and Modeling of Complex Structures in Solids: *Armen G. Khachaturyan*[1]; [1]Rutgers University, Ceram. & Matls. Engrg., 607 Taylor Rd., Piscataway, NJ 08502 USA

The significance of a transformation-induced strain for the thermodynamics of the phase transformations and will be discussed. This strain can qualitatively change the thermodynamics of coherent systems. The density function kinetic equations provide an efficient way to study the kinetics of microstructure evolution. Depending on the research objectives, the density functions can be either atomic densities or densities of compositional or structural parameters in nano- and meso-scales. For atomic scale simulations, the phenomenological density kinetic equations are formulated by an extension of the existing microscopic kinetic equations that assume atomic redistribution over underlying host lattice sites to more general cases where atomic positions are arbitrary. Examples of the application of these methods to the modeling of complex microstructure transformations at atomic and nano- scales will be discussed. It will be shown that the theory and models are already mature enough to realistically reproduce complex microstructures of different nature and even to predict new mechanisms of the microstructure transformation.

9:10 AM Invited
Elastic Domains and Khachaturyan's Phase Field Microelasticity Theory: *Alexander L. Roytburd*[1]; [1]University of Maryland, Matls. Sci. & Engrg., Coll. Park 20742 USA

Microstructural evolution in solids can be considered as combination of the coherent phase transformations and plastic deformations. The nucleation and movement of dislocations lead to relaxation of internal stresses and affect the thermodynamic and kinetic of phase transformations. The Khachaturyan's theory of microelasticity creates an effective and elegant tool for quantitative simulation of these interrelated microstructure mechanisms. On the other side, the concept of elastic domains with dislocation screening presents qualitative interpretation of simulation results. Both approaches will be discussed in the talk.

9:35 AM Invited
Self-Accommodation Mechanism of Thermoelastic Martensites: *Kazuhiro Otsuka*[1]; Takuya Ohba[2]; [1]National Institute for Materials Science, Advd. Matls. Lab., 1-1 Namiki, Tsukuba, Ibaraki 305-0044 Japan and Foundation for Advancement of International Science(FAIS), Tsukuba, Japan; [2]Shimane University, Dept. of Matls. Sci., Nishikawatsu, Matsue, Shimane 690-8504 Japan

All crystallogrphic characteristics, such as habit plane, orientation relationship etc., of martensitic transformations in most alloys can be described by the so-called "phenomenological crystallographic theory of martensitic transformations", in which the habit plane is treated as an invariant plane. Thus much of the strains arising from the martensitic transformation can be eliminated by the invariant plane strain condition. However, this mechanism cannot eliminate shear strains along the habit plane. Thus in order to eliminate strains further, two or four (in a special case may be three) habit plane variants are formed

side by side. This process is called self-accommodation. We will discuss the self-accommodation morphology of various martensites both experimentally and theoretically, which include B2-14M transformation in Ni-Al, B2-z2'(trigonal) transformation in Au-Cd, B2-R transformation in Ti-Ni-Fe and B2-B19 transformation in Ti-Ni-Cu. We also discuss a quite complicated case of B2-B19' (monoclinic) transformation in Ti-Ni.

10:00 AM
Crystallographic and Lattice Point Correlations of a New hcp-to-fco Martensitic Transformation in the Hf-Ni System: *J. H. Li*[1]; H. B. Guo[1]; *B. X. Liu*[1]; [1]Tsinghua University, Dept. Matl. Sci. & Engrg., Beijing 100084 China

Based on a newly constructed tight-binding Hf-Ni potential, molecular dynamics simulations reveal a new hcp-to-fco (face-centered orthorhombic) martensitic phase transformation in the Hf hcp-lattice, when the Ni solute atoms approach 19 at %, and the transformation speed is on the order of 100 m/s. The detailed mechanism of the martensitic phase transformation is figured out to involve the following four coinstantaneous movements: (1) sliding of (002) planes, (2) uniformly shearing on (010) planes along [010] directions, (3) stretching along [120] direction and (4) adjusting of the lattice constants in three principal crystalline axes of the resultant phase. After a series of analytical deduction, crystallographic constraints to the martensitic phase transformation and the corresponding matrix of lattice vectors between the initial hcp and final fco lattices are obtained, respectively, and they are also relevant for governing the possible hcp-to-bct (body-centered cubic) and hcp-to-fcc martensitic phase transformations.

10:15 AM Break

10:40 AM Invited
Incorporating Micromechanics into Phase Field Approach to Microstructure Evolutions in Complex Material Systems: *Yu U. Wang*[1]; [1]Virginia Tech, Matls. Sci. & Engrg., Blacksburg, VA 24061 USA

The problems of microstructure evolutions in complex material systems, such as multi-phase multi-domain microstructures, multi-dislocation and multi-crack ensembles, are discussed within the framework of Phase Field Microelasticity (PFM) theory. We consider different applications of PFM for modeling various processes by further developing the Khachaturyan's reciprocal space microelasticity theory. This is based on a new variational procedure that naturally incorporates micromechanics into the Phase Field approach. By using a virtual misfit strain field, the method efficiently solves the micromechanical problems involving arbitrary elastic modulus mismatch and crystal lattice misfit. Simulations of dislocation dynamics in bulk and thin films, crack propagations, surface roughening of heteroepitaxial films, phase transformations near free surface and in thin films are presented.

11:05 AM Invited
Phase Field Modelling of Transformation Strain Effect on Solid State Transformations: *Ingo Steinbach*[1]; Markus Apel[1]; [1]RWTH-Aachen, Access e.V., Intzestr. 5, Aachen D-52072 Germany

The ground breaking work of A. Khachaturyan and his co-workers on stress and strain effects on multiphase systems with coherent interfaces since more than one decade forms one pillar in Phase Field theory. Recently the principle model was generalized to treat elastically inhomogenous materials and it allows now to study effective elasticity in multigrain materials. In this presentation a multiphase field model is discussed, that follows the notion of the Khachaturyan model. Special emphasis is given to the elastic conditions in the diffuse interface between elastically different materials. It is demonstrated, how different interface conditions affect the elastic force on transformation in a multiphase system such as low carbon steel. An argument is derived for an 'optimal' model, that is applied to investigate nucleation and growth of ferrite into an austenite structure.

11:30 AM
Crystal Level Modeling of the Alpha to Epsilon Phase Transformation in Iron: *Nathan Barton*[1]; Richard Becker[1]; [1]Lawrence Livermore National Laboratory, PO Box 808, L-227, Livermore, CA 94551 USA

We present a crystal level model with phase transformation capabilities. The model is formulated to allow for large pressures (on the order of the elastic moduli) and makes use of a multiplicative decomposition of the deformation gradient in each constituent crystal. In this decomposition, elastic and thermal lattice distortions are combined into a single lattice stretch. This allows the model to be used in conjunction with general equation of state relationships. Within a given material element, phase transformations induce mass fraction rates between the constituents of the material. Deformation results from both these phase transformations and deformation of the constituents themselves. The driving force for phase transformations includes terms arising from mechanical work, from the temperature dependent chemical free energy change on transformation, and from interaction energy among the constituents. Simulation results are available for the alpha to epsilon phase transformation in iron. Results include simulations of shock induced transformation in single crystals and of compression of polycrystals. Results are compared to available experimental data. This work was performed under the auspices of the U.S. Department of Energy by University of California, Lawrence Livermore National Laboratory under Contract W-7405-Eng-48.

11:45 AM
"Burst-Like" Behavior During the Diffusionless Alpha Prime to Delta Transformation in a Pu-Ga Alloy: Kerri J.M. Blobaum[1]; *Christopher R. Krenn*[1]; Mark A. Wall[1]; Adam J. Schwartz[1]; [1]Lawrence Livermore National Laboratory, PO Box 808, L-353, Livermore, CA USA 94551

Phase transformations in plutonium alloys have many features that are difficult to model computationally. The transformation on cooling from δ to α' proceeds to less than 30% completion and has unusual double-c kinetics. A volume change of 20% during the transformation results in significant plastic deformation and a thermal hysteresis of 100K or more. Although 24 unique variants of α' phase are allowed, typically only 4 are seen to nucleate and grow in any given grain of δ. During the reversion back to δ at constant heating rates, unusual periodic "bursts" have been often observed, and the period appears to be independent of experimental technique and heating rate. We compare models of bursting caused by local elastic and thermal inhomogeneities, and conclude that plasticity induced residual stresses are the most likely explanation for the bursts. We also discuss general requirements for a complete computational model of this transformation.

12:00 PM
Severe Plastic Deformation and Deformation Twinning in NiTi Shape Memory Alloys: *Ibrahim Karaman*[1]; Ajay V. Kulkarni[1]; [1]Texas A&M University, Dept. of Mechl. Engrg., MS 3123, Coll. Sta., TX 77843 USA

In this study, thermomechanical properties of severely deformed Ti-50.8 at% Ni alloy using Equal Channel Angular Extrusion (ECAE) are investigated. Solutionized NiTi bars were deformed at different temperatures, i.e. room temperature which is above the austenite finish temperature (Af) and 450°C. The aim was to investigate the effects of ausforming (deformation above Af) on shape memory characteristics of NiTi such as superelasticity, transformation temperatures and fatigue properties. DSC was used to explore the effects of heat treatment temperature and time on the as-received, solutionized and as-deformed materials in terms of transformation temperatures, R-phase formation, and change in thermal hysteresis. TEM was utilized to reveal the changes in microstructure and formation of deformation twinning induced nanograins by in-situ heating and cooling experiment. Cyclic deformation tests are done on the as received, solutionized and as-deformed samples before and after some selected heat treatments. In this presentation improvement in thermal and mechanical properties with severe ausforming and subsequent annealing will be demonstrated. Stable cyclic response, pseudoelastic strain, change in transformation temperatures, formation of R-phase and nanograins, effects of precipitates will be rationalized with the observations on microstructures and possible deformation mechanisms. The unique microstructural findings were: 1) the observation of a mixture of heavily deformed B2 (austenite) and B19' (martensite) phases in the samples processed at room temperature although martensite stabilization was expected, 2) the observation of highly organized, twin-related nanograins in B2 phase of the samples deformed at room temperature, and 3) simultaneous observation of B2 austenite and strain induced B19' martensite in the samples deformed at 450°C. Strain-induced martensite in NiTi alloys was reported for the first time. The formation of well-organized twin-related nanograins via severe plastic deformation opens a new opportunity for twinning induced grain boundary engineering in NiTi alloys which is believed to improve cyclic stability and fatigue resistance of these alloys.

The Langdon Symposium: Flow and Forming of Crystalline Materials: Creep

Sponsored by: Materials Processing & Manufacturing Division, Structural Materials Division, MPMD-Shaping and Forming Committee, SMD-Mechanical Behavior of Materials-(Jt. ASM-MSCTS)

Program Organizers: Yuntian Ted Zhu, Los Alamos National Laboratory, Materials Science and Technology Division, Los Alamos, NM 87545 USA; P. B. Berbon, Rockwell Scientific Company, Thousand Oaks, CA 91360 USA; Atul H. Chokshi, Indian Institute of Science, Department of Metallurgy, Bangalore 560 012 India; Z. Horita, Kyushu University, Department of Materials Science and Engineering, Fukuoka 812-8581 Japan; Sai V. Raj, NASA Glenn Research Center, Materials Division, Cleveland, OH 44135 USA; K. Xia, University of Melbourne, Department of Mechanical and Manufacturing Engineering, Victoria 3010 Australia

Monday AM Room: 3024
February 14, 2005 Location: Moscone West Convention Center

Session Chairs: Michael E. Kassner, University of Southern California, Aeros. & Mechl. Engrg., Los Angeles, CA 90089-1453 USA; Atul H. Chokshi, Indian Institute of Science, Metall. Dept., Bangalore 560012 India; K. Linga Murty, North Carolina State University, Raleigh, NC 27695-7909 USA; Brian Wilshire, University of Wales Swansea, Matls. Rsch. Ctr., Sch. of Engrg., Singleton Park, Swansea SA2 8PP UK

8:30 AM
Contribution of Early Works by Terence Langdon in Modern Materials Science: *Ruslan Z. Valiev*[1]; Yuntian T. Zhu[2]; [1]Ufa State Aviation Technical University, Inst. of Physics of Advd. Matls., 12 K. Marx str., Ufa 450000 Russia; [2]Los Alamos National Laboratory, Matls. Sci. & Tech. Div., MS G755, STC, Los Alamos, NM 87545 USA

Prof. T.G. Langdon has been ranked as the second most cited author in materials science during the last 10 years by the international Institute for Scientific Information (ISI, Philadelphia, PA, USA). The analysis of his works shows that his most highly cited works are those dealing with recent studies of microstructural evolution and mechanical properties of ultrafine-grained (UFG) materials processed by severe plastic deformation, as well as earlier works on superplasticity carried out in the 1970-1980s. This paper traces how those early works have significantly affected the current investigations of the mechanical behaviour of UFG materials produced by severe plastic deformation.

8:45 AM
Rate-Controlling Processes in Creep of Subgrain-Containing Materials: *Oleg D. Sherby*[1]; Oscar A. Ruano[2]; [1]Stanford University, Matls. Sci. & Engrg., Stanford, CA 94305-2205 USA; [2]Centro Nacional de Investigaciones Metalurgicas, Dept. of Physl. Metall., CENIM, Av. Gregorio de Amo, 8, Madrid 28040 Spain

Polycrystalline materials that exhibit five-power-law creep behaviour are characterised by the presence of subgrains. In addition to the contribution of the subgrain-boundary as a barrier, it is also the source of the rate-controlling diffusion process in creep. It is proposed that the opposing stress fields, from the subgrain boundary and from the piled-up dislocations, will be relaxed by atom diffusion to allow climb of the lead dislocation in the pile-up. The atom diffusion process (solute or solvent) involves the combination of two edge dislocations in the subgrain boundary to form a double burgers vector (Smoluchowski) dislocation that releases the dislocation. The Smoluchowski dislocation reverts back to the prior two-dislocation structure during the climb of the dislocation(s) from the pile-up. It is a form of thermal-mechanical ratchetting. The model explains unusual creep behaviour in a number of metal systems.

9:00 AM
Deformation Mechanism Maps and Microstructural Influences: *Geoffrey Wilson Greenwood*[1]; [1]University of Sheffield, Dept. of Engrg. Matls., Sheffield UK

Areas on these maps define ranges, of homologous temperature and of applied stress divided by an elastic modulus, over which specific mechanisms of deformation are predominant. Langdon has illustrated their important features. The lines separating the mechanisms of overall sliding from those of diffusional drift are of particular significance but can be difficult to locate. It is shown how observations of microstructural features assist in this location and also provide extensive information on the way in which microstructure can influence the line positions. Notably, the flux patterns of diffusional drift are dependent upon the type of stress system superimposed as well as on microstructure. In many instances, the flux patterns can be determined to permit the evaluation of deformation rates.

9:15 AM
Grain and Grain Boundary Zone Contributions to Strain Accumulation During Creep of Polycrystalline Copper: *Brian Wilshire*[1]; Howard Burt[1]; Alun John Battenbough[1]; [1]University of Wales Swansea, Matls. Rsch. Ctr., Sch. of Engrg., Singleton Park, Swansea SA2 8PP UK

With pure metals, variations in the creep behaviour patterns displayed with decreasing applied stress are often interpreted in terms of a change from dislocation processes occurring entirely within the grains to boundary-dependent diffusional mechanisms which do not involve grain deformation. This transition is considered by reference to data obtained for pure polycrystalline copper, including the experimentally observed effects of grain size variations and of prestraining at room temperature. This evidence indicates the importance of distinguishing between the contributions made by the grain interiors and the grain boundary zones to the overall rates of strain accumulation at different stress levels.

9:30 AM
Effect of Temperature on Transitions in Creep Mechanisms in Class-A Alloys: *K. Linga Murty*[1]; Glenn T. Dentel[1]; Jeff C. Britt[1]; [1]North Carolina State University, PO Box 7909, Raleigh, NC 27695-7909 USA

Alloy class materials exhibit viscous glide controlled creep where dislocations are locked by solute atoms thereby decreasing their glide velocity while dislocation annihilation by climb still occurs. The creep-rate here varies as cube of the applied stress (n=3) while the activation energy for creep becomes equal to that for solute atom diffusion. At high enough stress, the dislocations get freed from solute atom locking and transition to climb controlled creep is noted with n~5 while at still higher stresses, power-law breakdown is observed. For relatively small grain-sizes, viscous creep mechanisms such as Nabarro-Herring or Coble creep usually occurs at low stresses. A close examination of the model equations reveals that at temperatures below a critical temperature, a transition from diffusional viscous creep to dislocation climb occurs without the intermediate viscous glide creep. Recent experimental results on a Zr-Nb sheet clearly follow these formulations exhibiting narrower intermediate region with decreasing temperature.

9:45 AM
Inhomogeneous Flow Characteristics in Plastically Accommodated Creep of a Composite: *Eiichi Sato*[1]; Kenshi Kawabata[2]; Kazuhiko Kuribayashi[1]; [1]Institute of Space and Astronautical Science/ Japan Aerospace Exploration Agency, 3-1-1 Yoshinodai, Sagamihara, Kanagawa 229-8510 Japan; [2]Nagaoka University of Technology, Dept. of Mechl. Engrg., 1603-1 Kamitomioka, Nagaoka, Niigata 940-2188 Japan

During high-temperature creep of a composite consisting of matrix and reinforcements, if diffusional accommodation is not sufficient, the strain mismatch between the matrix and inclusions must be accommodated by inhomogeneous flow of the matrix, called as "plastic accommodation". Unlike room temperature deformation showing work hardening, steady-state, plastically-accommodated creep might be inhomogeneous in space, but might not yield the rotation of the matrix lattice. This paper present, for the first time, the direct observation of inhomogeneous deformation without lattice rotation in a crept Ti/TiB(w) composite in plastic accommodation condition. Inhomogeneous flow was observed by the deposited AgPd and lattice rotation was observed by EBSP on the polished surface. The nature of plastically accommodated creep is then discussed.

10:00 AM
Compression and Tensile Creep of Binary NiAl: *S. V. Raj*[1]; [1]NASA Glenn Research Center, Matls. Div., MS 106-5, 21000 Brookpark Rd., Cleveland, OH 44135 USA

Compression creep and long term tensile creep studies were conducted on cast and extruded binary NiAl in the temperature range 700-1200 K with the objectives of characterizing and understanding the creep mechanisms dominant in this alloy. Inverse and normal primary creep curves were observed in both compression and tension creep depending on stress and temperature although an asymmetrical response was observed under these two stress states. It was concluded that the primary creep of NiAl is limited by dislocation mobility. The stress exponents, n, for compression and tensile creep were similar varying between about 5 and 14. However, there were significant differences in the stress dependence of the activation energies for com-

pression and tensile creep. The true activation energy for tensile creep, Qc, was constant and equal to about 400 kJ mol-1 between 20 and 50 MPa but decreased to a constant value of 250 kJ mol-1 between 50 and 110 MPa. The activation energy was observed to be inversely stress dependent above 110 MPa. In contrast, Qc ≈ 300 kJ mol-1 for compression creep was constant between 25 and 70 MPa and inversely dependent on the true stress above 70 MPa. A detailed discussion of the probable dislocation creep mechanisms governing compressive and tensile creep of NiAl is presented. It is concluded that the non-conservative motion of jogs on screw dislocations influenced the nature of the primary creep curves, where the climb of these jogs involves either the next nearest neighbor or the six-jump cycle vacancy diffusion mechanism. The probable natures of the atom-vacancy exchange that occur within the core of an edge dislocation undergoing climb in NiAl are schematically examined.

10:15 AM
Creep Behaviour of Mg Alloys and Composites Investigated by Acoustic Emission: *Frantisek Chmelik*[1]; Zuzanka Trojanova[1]; Pavel Lukac[1]; [1]Charles University, Dept. of Metal Physics, Ke Karlovu 5, Praha 2 12116 Czech Republic

The application of different processing has allowed preparing magnesium-based materials with different grain size. The creep tests were conducted in the temperature range of 423-473 K under stress between 30 and 95 MPa. Acoustic emission was monitored during the test. The results demonstrate that the preparation technique can influence the creep behaviour. In the case of composites, the creep behaviour depends on the reinforcement and the matrix alloy. The analysis of the creep data of unreinforced alloys shows an increase in the stress exponent and an increase in the activation energy. No clear dependence of the stress exponent and the activation energy on temperature and applied stress is observed for composites crept at similar conditions. The acoustic emission activity is higher in the composite and it depends on the reinforcement. Acoustic emission indicates the initiation of failure earlier than that observed on the creep curve.

10:30 AM Break

10:45 AM
Recent Developments in Mechanisms of Five Power-Law Creep: *M. E. Kassner*[1]; [1]University of Southern California, Aeros. & Mechl. Engrg., OHE 430, CA 90089-1453 USA

This work will describe the latest developments on the understanding of the dislocation mechanisms for elevated temperature five power-law creep in materials. This will include a recent analysis of the applicability of the classic Taylor-hardening equation to creep in this regime. Additionally, there will be a discussion of the latest developments in the assessment of internal stresses in creep, including x-ray peak asymmetry analysis.

11:00 AM
Analysis, Representation, and Prediction of Creep Transients in Class I Alloys: *Eric M. Taleff*[1]; W. Paul Green[1]; Terrry R. McNelley[2]; Paul E. Krajewski[3]; [1]University of Texas, Dept. of Mechl. Engrg., 1 Univ. Sta., C2200, Austin, TX 78712-0292 USA; [2]Naval Postgraduate School, Dept. of Mechl. Engrg., 700 Dyer Rd., Monterey, CA 93943-5146 USA; [3]General Motors Corporation, R&D Ctr., Bldg. 1-6, 30500 Mound Rd., Warren, MI 48090-9055 USA

Solute-drag creep in Class I alloys, also known as Class A alloys, is characterized by several features. Among these is the presence of "inverse" creep transients, which is a feature unique to these solid-solution alloys and the solute-drag creep mechanism. These creep transients can involve large changes in flow stress that occur over extended periods of strain and may have substantial impact on commercial hot-forming operations. A graphical construct for conveniently representing the magnitudes of creep transients, in general, and inverse transients, in particular, has been recently proposed. The present investigation develops methodology, based on the graphical construct, for the representation, analysis, and prediction of creep transients, with special emphasis on the inverse transients of Class I alloys.

11:15 AM
Impression Creep of a Mg-8Zn-4Al-0.5Ca Alloy: Lingling Peng[2]; *Fuqian Yang*[2]; Jian-Feng Nie[3]; James C.M. Li[1]; [1]University of Rochester, Dept. of Mechl. Engrg., Rochester, NY 14627 USA; [2]University of Kentucky, Dept. of Chem. & Matls. Engrg., Lexington, KY 40506 USA; [3]Monash University, Sch. of Physics & Matls. Engrg., Victoria Australia

The creep behavior of a precipitation hardenable Mg-8Zn-4Al-0.5Ca (wt%) casting alloy was determined by using the impression technique in the temperature range 403-623 K and under a punching stress between 1.68 MPa at 623 K and 60.4 MPa at 403 K. The alloy was solution treated for 4 hours at 325°C, water quenched and subsequently aged for 16 hours at 200°C (peak-aged) before the impression tests. Using a power law between the impression velocity and the punching stress, the activation energy is a function of the punching stress and changes from 75.3 kJ/mol at 6.71 MPa to 39.2 kJ/mole at 53.6 MPa. However, by using a hyperbolic sine function between the steady-state impression velocity and the punching stress, a single activation energy is found to be 76.5 kJ/mole, which is about half of the activation energy for lattice diffusion in Mg, 134-139 kJ/mole as summarized by Fujikawa.[1] It suggests that a single mechanism such as grain boundary fluid flow could be rate controlling. This research is supported by NSF through DMR-0211706 monitored by Drs. Guebre Tessema and Bruce A. MacDonald and the Kentucky Science and Engineering Foundation through KSEF-148-502-03-73. [1]S.-I. Fujikawa "Diffusion in Mg" Qin Jin Shu (Light Metals) 42, 822-825 (1992) (in Japanese).

11:30 AM
Predicting Harper-Dorn Creep Rates Using Data on Static Recovery: *Marek A. Przystupa*[1]; Yi Tan[1]; Alan J. Ardell[1]; [1]University of California, Dept. of Matls. Sci. & Engrg., Los Angeles, CA 90095 USA

One of the distinctive features of the dislocation network theory of Harper-Dorn (H-D) creep is that it is capable of predicting steady-state creep rates based only on the knowledge of (1) the steady-state dislocation density and (2) the rates of static recovery of the network. Until now these predictions could not be rigorously tested because of the notorious lack of the high temperature data on static recovery for all materials tested in the H-D creep regime. In this talk we will present our recent high-temperature data on static recovery for polycrystalline aluminum. We show how the data can be used to obtain the important parameters in the dislocation network theory of H-D creep and subsequently used to predict the creep behavior. The resulting predictions of the H-D steady-state creep rates will be then compared with experimental measurements obtained by us and others, as well as with the predictions of the edge dislocation climb model under vacancy-saturated conditions developed over the years by Professor Langdon and his associates.

11:45 AM
Harper-Dorn Creep in Metals at Intermediate Temperatures Revisited: *Lubos Kloc*[1]; Jaroslav Fiala[2]; [1]Academy of Sciences of the Czech Republic, Inst. of Physics of Matls., Zizkova 22, Brno CZ-61662 Czech Republic; [2]Brno University of Technology, Faculty of Chmst., Purkynova 118, Brno CZ-61200 Czech Republic

Harper-Dorn creep, that is creep with apparent stress exponent close to one and independent of grain size have been observed in many metallic materials at temperatures close to the melting point of the material. Moreover, some observations of the similar behavior at intermediate temperatures of about a half of the melting point were interpreted as a "intermediate temperature" Harper-Dorn creep. The micromechanisms behind Harper -Dorn creep were a matter of large debate, but with no clear result. The stress and temperature dependencies of the creep rates derived from the constant stress, constant temperature experiments and ignoring transient "constant structure" effects in fact do not reflect the behavior of underlying micromechanisms directly. The previous results of intermediate temperature H-D creep are reinterpreted and completed with new observations to show that the direct relation between apparent stress exponent and micromechanisms involved in the deformation process is misconception.

12:00 PM
Creep Behavior of Mg-Al Alloys and its Comparison with Al-Mg Aalloys: *Woo-Jin Kim*[1]; Ho-Kyung Kim[2]; [1]Hong-Ik University, Dept. of Matls. Sci. & Engrg., 72-1 Sangsu-dong, Mapo-gu, Seoul 121-791 S. Korea; [2]Seoul National University of Technology, Dept. of Auto. Engrg., 172 Kongnung-dong, Nowon-gu, Seoul 139-743 Korea

Creep behavior of coarse and fine grained Mg-Al alloys (AZ31) was investigated in a wide strain rate (2x10-7 ~ 7x10-2 s-1) and temperature range (443K ~ 823K) using double shear creep and tensile testing methods. Viscous glide controlled creep, dislocation climb creep and grain boundary sliding arose as the flow rate-controlling process. Effect of temperature, stress, alloying content and grain size on the transition of deformation mechanism was specially focused. The results were compared with those of the Al-Mg alloys of which creep behavior was well-known. The effects of Al addition to Mg and Mg addition to Al on solid drag creep were compared and discussed.

12:15 PM
Role of Grain Boundary Sliding in Creep of Sn-Rich Solder Alloys: Felipe Ochoa[1]; Xin Deng[1]; *Nik Chawla*[1]; [1]Arizona State Uni-

versity, Dept. of Cheml. & Matls. Engrg., Fulton Sch. of Engrg., Tempe, AZ 85287 USA

The creep behavior of Sn-rich solder alloys is controlled by two major creep mechanisms: (a) Thermally-induced climb of dislocations over fine intermetallic particles (such as Ag3Sn) and (b) grain boundary sliding (GBS). In this talk, we report on a systematic study on the role of GBS in creep of bulk Sn-3.5 wt% Ag solder alloys at 60°C and 120°C. The solder microstructure was varied by cooling at two different rates: 24°C/s (finer microstructure) and 0.08°C/s (coarser microstructure). Fiducial lines were inscribed on the solder surface and creep tests were interrupted to quantify the evolution of microstructure and strain due to GBS. The microstructure evolution due to creep deformation was characterized using atomic force microscopy (AFM) and scanning electron microscopy (SEM). Measurements of the transverse offset in the fiducial marks twere carried out and the strain due to GBS was quantified. It will be shown that, in general, the strain due to GBS is quite inhomogeneous and is a small fraction of the total creep strain (in the primary and steady-state creep regimes), although the contribution of GBS varies with temperature and microstructure. A comparison of the Sn-rich alloy behavior with that of Pb-Sn alloys (by Langdon and co-workers) will be presented.

6th Global Innovations Symposium: Trends in Materials and Manufacturing Technologies for Transportation Industries: Keynote Session

Sponsored by: Materials Processing and Manufacturing Division, MPMD-Computational Materials Science & Engineering-(Jt. ASM-MSCTS), MPMD-Nanomechanical Materials Behavior, MPMD-Phase Transformation Committee-(Jt. ASM-MSCTS), MPMD-Powder Materials Committee, MPMD-Shaping and Forming Committee, MPMD-Solidification Committee, MPMD-Surface Engineering Committee, MPMD/EPD-Process Modeling Analysis & Control Committee

Program Organizers: Thomas R. Bieler, Michigan State University, Department of Chemical Engineering and Materials Science, East Lansing, MI 48824-1226 USA; John E. Carsley, General Motors Corp, Warren, MI USA; Hamish L. Fraser, Ohio State University, Department of Materials Science and Engineering, Columbus, OH 43210-1179 USA; John E. Smugeresky, Sandia National Laboratories, Department 8724, Livermore, CA 94551-0969 USA

Monday PM Room: 2009
February 14, 2005 Location: Moscone West Convention Center

Session Chairs: Thomas R. Bieler, Michigan State University, Dept. of Cheml. Engrg. & Matls., E. Lansing, MI 48824 USA; Hamish L. Fraser, Ohio State University, Dept. of Matl. Sci. & Engrg., Columbus, OH 43210 USA

2:00 PM Keynote
Automotive Research: Technical Trends and Challenges: *Alan Taub*[1]; [1]General Motors Corporation, R&D & Planning, Warren, MI 48090 USA

The population of the earth stands above 6.3 billion people today and in another 15 years will approach 7.5 billion. As world population rises, vehicle ownership is also expected to climb dramatically. In order to sustain increasing numbers of vehicles, the automotive industry must address important challenges in several key areas: energy, emissions, safety, congestion, and affordability. This talk will cover General Motors' current strategies on how to address these challenges, highlighting developments in advanced propulsion, vehicle electronics, lightweight and smart materials, and agile manufacturing. These technologies are key to enable the industry to extend the significant benefits of personal mobility to people around the globe.

2:30 PM Keynote
Materials and Manufacturing Challenges for the 21st Century Vehicles: *Subi Dinda*[1]; [1]DaimlerChrysler Corporation USA

Increased demands on safety and fuel economy for future automobiles require innovative technologies for cost effective applications of materials and manufacturing processes. This presentation highlights the strategy of new material applications coupled with novel manufacturing processes at DaimlerChrysler. Rapid emergence of new material demands equally rapid development of cost effective manufacturing processes. The challenges faced by the automotive industry in managing competing priorities of cost reduction, lightweighting, safety enhancement, and customer features will be discussed.

3:00 PM Keynote
Enabling, Enhancing, Empowering - The Role of Propulsion Materials Technologies in the Aerospace Industry: Daniel F. Paulonis[1]; *John J. Schirra*[1]; [1]Pratt & Whitney, 400 Main St., MSC 114-40, E. Hartford, CT 06108 USA

The aerospace industry is in the midst of unprecedented business drivers that have the potential to change its fundamental structure. After experiencing losses of $25B since the beginning of the new century, the industry is restructuring for sustainable, investable growth. Materials technologies will play a key role in this recreation as they enable advances in engine efficiency through increased operating temperatures and higher rotational speeds. Enhancements to airline profitability will be achieved through implementation of lower cost manufacturing processes for spare parts and more effective repair methods. Integration of advanced engineering tools with material damage evolution mechanisms will empower airlines to increase the safe and reliable utilization of their assets while planning for required maintenance. These objectives will be accomplished through sustained investment in fundamental materials research with a focus on engineering solutions, through the use of industry wide collaborative efforts and the implementation of dual use technologies.

3:30 PM Break

3:45 PM Keynote
The Hydrogen Economy - Materials Challenges and Opportunities: *James A. Spearot*[1]; [1]General Motors Corporation, R&D, Warren, MI 48090 USA

Recent debate in both government and technical forums has focused on the value, the possibility, and the timing of meeting future transportation fuel demands by use of hydrogen generated from renewable sources of primary energy. The justifications for and the criticisms against development of renewable energy supplies and hydrogen-fueled propulsion systems are reviewed, and the technical hurdles to be overcome in creating such a future vision are identified. If the vision of a hydrogen-fueled transportation system is to become reality, significant material inventions and developments will be required. The opportunities for critical materials research programs in the areas of hydrogen generation, fuel cell development, and hydrogen storage are described. The status of General Motors' progress in development of hydrogen-fueled, fuel cell-powered vehicles is used to demonstrate the potential that a clean, renewable-hydrogen fuel-based transportation system can provide in meeting societal goals.

4:15 PM Invited
An Overview of Hydrogen Storage for Transportation Applications: *James C.F. Wang*[1]; [1]Sandia National Laboratories, Livermore, CA USA

Hydrogen storage has been one of the highest technical priorities of the DOE Office of Hydrogen, Fuel Cells and Infrastructure Technologies (HFCIT). Currently, no storage technologies meet the hydrogen vehicle requirements. New materials and/or new technical approaches are needed to meet the DOE FreedomCAR hydrogen storage goals for 2010 and 2015. This paper will present an overview of current hydrogen storage technologies and some of the new developments underway in national laboratories, universities and industrial companies. A brief description of Sandia led DOE Center of Excellence for Metal Hydrides will also be presented.

Alumina and Bauxite: Bayer Process Chemistry: Part II

Sponsored by: Light Metals Division, LMD-Aluminum Committee

Program Organizers: Dag Olsen, Hydro Aluminium AS, Porsgrunn 3907 Norway; Travis Galloway, Century Aluminum, Hawesville, KY 42348 USA; Halvor Kvande, Norsk Hydro ASA, Oslo N-0240 Norway

Monday PM Room: 2005
February 14, 2005 Location: Moscone West Convention Center

Session Chair: Robert Bitsch, Alcan, Bauxite & Alumina, Cedex, Gardanne, 13541 France

2:00 PM
Microstructure and Adsorption Behaviour of Sodium Aluminosilicate Polytipes in Sodium Aluminate Liquors: *Jonas Addai-Mensah*[1]; Jun Li[1]; Marek Zbik[1]; William Wilmarth[2]; [1]University of South Australia, Ian Wark Rsch. Inst., Mawson Lakes BLV, Mawson

Lakes, Adelaide, SA 5095 Australia; [2]Westinghouse Savannah River National Laboratory, Savannah River Tech. Ctr., Aiken, SC 29808 USA.

Sodium aluminosilicate (SAS) precipitation from SiO2-supersaturated sodium aluminate solution commonly occurs in alumina refining and high level nuclear waste (HLNW) liquor processing industries. In alumina plant heat exchangers, the precipitation of SAS dimorphs (sodalite and cancrinite) from spent liquors leads to unwanted fouling, impacting dramatically on heat transfer efficiency, liquor throughput and production costs. SAS precipitation fouling of HLNW evaporators may result in radionuclides (e.g. uranium) incorporation, posing a serious criticality concern and additional, technological processing challenge. In the present work, the micro and crystallo-chemical structures of four SAS polytypes (amorphous, zeolite A, sodalite and cancrinite) were determined and correlated with their solution uranium species adsorption behaviour. It was established that SAS phase-specific micro and crystallo-chemical structures play pivotal roles in uranium loading. Under similar conditions, the amorphous phase showed the greatest uranium uptake, with micro/mesoporosity being an important factor governing uranium loading for all 4 SAS adsorbents.

2:25 PM
Polymers as Anti-Scaling Materials in the Bayer Process: *Eoin P. Enright*[1]; Kenneth T. Stanton[1]; John Haines[2]; Teresa Curtin[1]; [1]University of Limerick, Matls. & Surface Sci. Inst., Natl. Technogl. Park, Limerick Ireland; [2]Aughinish Alumina Ltd., Aughinish Island, Askeaton, Co. Limerick Ireland

Scaling within the Bayer process is a widespread problem both in terms of cost of removal and the human risk associated with de-scaling operations. Here we present an overview of the possible use of polymer surfaces in anti-scaling applications. Various strategies may be employed including the use of materials as coatings that either do not scale or have a weak bond at the scale interface such that scale shedding is frequent and predictable. Preliminary results are shown from plant-based experiments where several representative polymeric materials were exposed to the liquor stream in a decanter overflow and scaling rates were measured. Degradation characteristics of these materials in Bayer liquor has been measured using Raman and Fourier-Transform Infrared (FT-IR) spectroscopy and these results are presented and discussed. Microscopy and X-ray analyses are also given.

2:50 PM
Reagents for the Elimination of Sodalite Scaling: Donald Spitzer[1]; Alan Rothenberg[1]; Howard Heitner[1]; Frank Kula[1]; *Morris Lewellyn*[1]; Owen Chamberlain[1]; Qi Dai[1]; Calvin Franz[1]; [1]Cytec Industries, 1937 W. Main St., Stamford, CT 06904 USA

Reagents have been discovered that can greatly reduce or even completely eliminate sodalite scaling in heat exchangers, pipes, etc. in lab, pilot plant, and plant tests. Most importantly, these results are achievable at practical dosages. Extensive downstream testing has not shown any negative effects even in the unlikely event that the reagents get through to precipitation. The reagents are, in fact, adsorbed onto red mud solids and should not accumulate in the circuit.

Alumina and Bauxite: HES and Control & Modelling

Sponsored by: Light Metals Division, LMD-Aluminum Committee
Program Organizers: Dag Olsen, Hydro Aluminium AS, Porsgrunn 3907 Norway; Travis Galloway, Century Aluminum, Hawesville, KY 42348 USA; Halvor Kvande, Norsk Hydro ASA, Oslo N-0240 Norway

Monday PM Room: 2005
February 14, 2005 Location: Moscone West Convention Center

Session Chair: Jean-Pierre Riffaud, Alumina Partners of Jamaica, Manchester, Jamaica W. Indies

3:15 PM
Studying So2 Emissions in the Calcination Area at Alumar: *Antonio Henrique S. P. Morais*[1]; *Valerio Araujo Gomes*[1]; *Aline Michelle O. Veloso*[1]; *Jonas Uizes Oliveira*[1]; *Julio C. Diniz Costa*[1]; [1]Consórcio de Alumínio do Maranhão - Alumar, EHS, BR-135, Km 18, Estiva, São Luís, Maranhão 65095-050 Brasil

One of the biggest environmental challenges in Alumina Refineries is the air emissions abatement. A proposed production increasing in calcination poses an obvious concern regarding future air emissions, such as SO2, due to the increase in heavy oil consumption. In order to comply with Brazilian regulations and to be aligned to the Alcoa 2020 Environmental Strategy a process evaluation throughout a mass balance was proposed to find out the total %S retained in the Alumina. and the stack emissions rate. The mass balance consisted of isokinetics samplings in the calciner stack, and simultaneously continuous control and measurement of all process parameters such as heavy oil consumption, alumina production, ESP Dust production and the %S in all lines. The main objective was to present the %S absorbed in the Alumina in the direct contact with flue gases and to provide information on which alternative for SO2 abatement should be chosen.

3:40 PM Break

3:55 PM
Experience with 3 x 4500 TPD Gas Suspension Calciners for Alumina: *Jens Fenger*[1]; Charles Wind[1]; Benny E. Raahauge[1]; [1]FFE Minerals Corporation, 77 Vigerslev Alle, Valby 2500 Denmark

In 2001, Queensland Alumina, Australia, launched their environmentally driven expansion project of replacing nine (9) rotary kilns by installing three (3) Gas Suspension Calciners, (GSC), each with a capacity of 4500 TPD. This was the first Calcination Plant ever, for Alumina, in which Stationary Calciners was equipped with Bag Houses for gas cleaning. The commissioning and project experience of the world largest Calcination Plant for Alumina and its impact on the environment will be presented.

4:20 PM
Improved Health and Safety Conditions and Increased Availability in Large Alumina Calcining Units: Hans W. Schmidt[1]; Michael Stroeder[1]; Gajendra Singh[2]; Marcilio Santana[2]; Joaquim Ribeiro[2]; Mike Cable[3]; John Priestrzeniewcz[3]; [1]Outokumpu Technology GmbH, Aluminium Business Sector, Ludwig-Erhard-Str. 21, Oberursel 61440 Germany; [2]Alumina do Norte do Brasil S/A, Km 12 Bacarena - PA Brazil; [3]Worsley Alumina Pty Ltd, Collie, WA Australia

Many existing alumina refineries are being expanded to capacities of more than 3 Mtpy and even up to 4.5 Mtpy. This requires the installation of larger calcination units for economic and operational reasons. For today's alumina calciners the requirements for health protection are on a significantly higher level than 5 years ago. This paper explains how these requirements can be met and in particular what measures can be taken to reduce the level of noise, vibration, heat radiation and dust emission to meet current occupational health and safety standards. At the same time ergonomics has been taken into account. Normal operation, process disturbances and scheduled shut downs of the calciners require diligent process safety attention e.g. for combustion control and dust management. These issues are considered in a HAZOP analysis and subsequently incorporated in operating and maintenance procedures. Whilst over the past decade calcination plants producing 2000 to 2200 tpd represented the largest available units, today typical capacities are in the range of 3000 to 4500 tpd. To maximize the economic value of such large units, the availability factor is one of the most important issues. This paper describes measures to increase the availability factor of these large calcination units to more than 95%. To achieve this, the areas of partial load operation, refractory design, and lifetime of mechanical equipment have been improved and the trip sensitivity and number of moving parts in the calcination system have been decreased.

4:45 PM
Model-Based Digester Temperature Control at Alumina Partners of Jamaica Refinery: *Astley Vincent Forrester*[1]; *Terry Snow*[2]; [1]Alumina Partners of Jamaica, Techl. Dept., PO Box 529, Arabi, LA 70032-529 USA; [2]Comalco Alumina Refinery - Gladstone, Advd. Control, PO Box 1479, Gladstone, Queensland 4680 Australia

The Alpart Alumina Refinery in Jamaica, a Kaiser high temperature design, is a high-energy consumer relative to other plants of similar design. As one part of the energy improvement program a digester temperature control improvement project was implemented with significant improvement in energy consumption. A model-based temperature controller was designed and successfully implemented. The form of the controller is Feed-Forward Predictive with IMC in parallel form for dead-time compensation of model error. Extensive use was made of dynamic simulation using the Simulink system to design and tune the control strategy. The control strategy was found to be robustly stable to various forms of severe process disturbances.

5:10 PM
Application of Advanced Control to Digestion in a Bayer Circuit: *Horace Lawrence*[1]; *Robert K. Jonas*[2]; [1]WINDALCO, Kirkvine Works, Kirkvine PO, Manchester Jamaica; [2]Honeywell, Process Solutions, 2500 W. Union Hills, MS: M15, Phoenix, AZ 85023 USA

Plant operations have been implementing advanced control techniques in the mineral processing industry for several years now. The Bayer process used for alumina refinery is no exception to this, with multivariable predictive control and expert systems being the preferred technologies for increasing throughput and reducing costs. Ultimately this is achieved by exploiting the installed distributed control system (DCS) infrastructure of the refinery. Other potential benefits that a user can get by installing such systems include having a consistent response to process changes and the continuous optimization of the process. This paper discusses the successful application of multivariable predictive control to the digestion circuit at Windalco's Kirkvine Works, what the benefits were and how this technology could be applied to other sections in the Bayer process.

5:35 PM
Mathematic Models of the Seed Precipitation Process of Sodium Aluminate Solution: Liu Chang Qing[1]; Zhang Ping Min[1]; Chen Qi Yuan[1]; Yin Zhou Lan[1]; [1]Central South University, Coll. of Chmst. & Cheml. Engrg., Changsha City, Hunan Province 410083 China

The computer-based process control take a key part in the communication, digitalization, and automatization of alumina production. It is a mathematic model depicting the relations of various factors that affect the alumina production process. Based on the theory of secondary nuclearation and agglomeration dynamics, alumina production process was analyzed. In the "two stages" sand alumina hydroxide production process, the mathematic model of agglomeration process in the "first stage" and secondary nuclearation process in the "second stage" were obtained respectively.

Aluminum Reduction Technology: Cell Development & Operations - Part 1

Sponsored by: Light Metals Division, LMD-Aluminum Committee
Program Organizers: Tor Bjarne Pedersen, Elkem Aluminium ANS, Farsund 4551 Norway; Tom Alcorn, Noranda Aluminum Inc., New Madrid, MO 63869 USA; Halvor Kvande, Norsk Hydro ASA, Oslo N-0240 Norway

Monday PM Room: 2003
February 14, 2005 Location: Moscone West Convention Center

Session Chair: Knut Arne Paulsen, Hydro Aluminium, Karmøy Primary Production, Karmøy N-4265 Norway

2:00 PM
Current Efficiency in Prebake and Soderberg Cells: *Gary P. Tarcy*[1]; Knut Torklep[2]; [1]Alcoa, Inc, Hall Process Improvement, Alcoa Techl. Ctr., 100 Techl. Dr., Alcoa Ctr., PA 15069 USA; [2]Elkem Aluminium Research, Fiskaaveien 100, N-4621, Kristiansand Norway

An isotope dilution technique was used to study 24 h current efficiency in 22 semi-randomly selected prebake pots and 21 randomly selected Soderberg pots at the Elkem smelters. A total of 110 measurements were made and compared with the 1128 current efficiency measurements made on Alcoa prebake pots using Alcoa's silver dilution technique. Results are discussed with emphasis on similarities and dissimilarities in prebake and Soderberg. Some theoretical proposals are made regarding the similarities and differences. Results for the prebake pots confirm the basic conclusions from the Alcoa studies including the relative importance of bath chemistry compared to noise (instability) and the impact of low alumina operation on current efficiency. Measurements of 24 h current efficiencies for Soderberg pots are scarce to non-existent. Only temperature and aluminium fluoride have similar influences in the two pot technologies.

2:25 PM
Automated Positioning of Prebaked Anodes in Electrolysis Cells, Part 2: *Jean-Pierre Gagné*[1]; Marc-Andre Thibault[1]; Robin Boulianne[1]; Gilles Dufour[2]; Claude Gauthier[2]; [1]STAS, 1846 Outarde, Chicoutimi, Quebec G7K 1H1 Canada; [2]Alcoa Canada, 1 Place Ville Marie, Montreal, Quebec Canada

During the production of aluminum, the anodes used in electrolysis cells have to be replaced frequently. Even with obtained the best trained operating crew, such operation - given the number of people involved and the methods that are used - is prone to variability and lack of consistency. STAS and Alcoa Canada have been working on developing an automated system for the vertical positioning of anodes in electrolysis cells. At the 2004 TMS Annual Meeting, the first part of this article was presented and the works related to the development and testing of three particular methods were explained. Further to these works, tests were carried out on 36 pots over a time frame of 49 days using one automatic method. The main objective was to verify the effects of this method on the electrolysis process and the reliability of the system. In this paper, we will describe this trial period.

2:50 PM
Anode Height Adjusted Automatically by PTM: *Carlos Adriano Barcellos de Jesus*[1]; [1]Alumar, Pot Rooms, BR 135, km 18, Distrito Industrial de Pedrinhas, São Luís, MA 65095-050 Brasil

Since Alumar start up, anode setting has been a big issue due to safety and hygiene concerns and also due to high level of extra sets. Aiming to carry out theses tasks, Alumar decided to fully reevaluate its anode setting system. Starting from this study Alumar has decided to implement a project which allows automatic anode height adjustment by the pot tending machine (PTM). The system to adjust anode height from the ECL crane cabinet consists basically on an encoder at the crane anode extractor, which converts the extractor movements into electric pulses. The results of this project have shown improvement in the safety and hygiene conditions to pot operator as well as a strong reduction in early anode failures.

3:15 PM
Pre-Heating Optimization Study of Smelting Cells: *Carlos Eduardo Zangiacomi*[1]; Victor Carlos Pandolfelli[2]; Leonardo Paulino[3]; Stephen J. Lindsay[4]; Halvor Kvande[5]; [1]Alcoa Aluminum, Reduction/ Potlining, Rodovia Pocos-Andradas, km 10, Poços de Caldas, Minas Gerais 37701-970 Brazil; [2]Universidade Federal de Sao Carlos, Matls. Sci. & Engrg., Rodovia Washington Luis, km 235, Sao Carlos 13565-905 Brazil; [3]Alcoa Aluminum, Process Engrg./Smelter, Rodovia Pocos-Andradas, km 10, Poços de Caldas, Minas Gerais 37701-970 Brazil; [4]Alcoa Aluminum, Primary Metals, 300 N. Hall Rd., TN 37701-2516 USA; [5]Hydro Aluminum, Drammensveien 264, Oslo, NO NO-0240 Norway

In this paper the author will present data taken from studies performed at Alcoa Poços de Caldas VSS smelter in Minas Gerais, Brazil. The objective of the study was to gain a sufficient grasp of the phenomena taking place during the preheating of a Hall-Heróult cell and then determine the optimum preheating rate and total preheating time required for a better operating performance of the reduction cells. The basis for the work was built upon cathode pre-heating best practices that have been published by Halvor Kvande. In these studies differential temperatures have been compared over time for surface mounted and sub-cathodic thermocouples by using a rigorous numerical-experimental Factorial Test analysis. The author offers conclusions on the experiment test and provides the systemic approach that will address the behavior of other relevant materials leading to the optimized preheating curve.

3:40 PM Break

3:55 PM
Line II Restart Process at ALUMAR - Brazil: *Agnello J.A. Borim*[1]; Eliezer Batista[1]; Elisio Bessa[1]; Sérgio Matos[1]; [1]Consórcio de Alumínio do Maranhão, Potrm., Br 135, Km 18 - Distrito Industrial de Pedrinhas, São Luís, Maranhão 65095-604 Brazil

On July 18, 2003 a flashover occurred at Alumar Line II rectifier room, causing a major blow up and fire which completely destroyed rectifier 23. The adjacent rectifier 22 and the whole control room and cabling system were severely damaged. It is known that both rectifiers had been operating at their nominal capacity until it occurred. As a result of the event, all the pots from line II had to be cut out. Some of them were tapped, but others had all the metal frozen in. So, this big variability of frozen metal layer into the pots was an issue that Alumar had never faced. This paper describes the root causes of the accident, the alternatives to recover the rectifiers, strategies to minimize the production losses under the new rectifier capacity and key aspects to restart the pots as fast as possible and with no incidents.

4:20 PM
The Use of Transversal Slot Anodes at Albras Smelter: *Ronaldo Raposo de Moura*[1]; Hânderson Penna Dias[2]; [1]Albras, Carbon Plant, Rodovia PA 483 Km 21 - Vila Murucupi, Barcarena, Pará 68.447-000 Brazil; [2]Albras, Potlines III & IV, Rodovia PA 483 Km 21 - Vila Murucupí, Barcarena, Pará 68.447-000 Brazil

The present article discusses the results obtained at Albras potlines with transversally slotted anodes. It is commonly believed in smelters that longitudinal oriented slots are more beneficial in pot operation when compared to transversal slots. However, due to the Albras green anode compactor design it was only possible to make longitudinal slots by cutting the anodes after baking. In 2002 Albras started experimenting the slotted anodes of both types in a few pots. As a result the use of

transversal slotted anodes was extended to two 30 pots sections. Data obtained over a period of six months on real pot resistance, anode effect frequency, anode deformation (spikes), noise, anode scrap levels and butt cracking incidence are presented and analyzed. Observations are made on how spike formation may be avoided. Finally the savings and benefits obtained from the use of this type of anode are evaluated.

Applications and Fundamentals of High Aspect Ratio Nanomaterials: Simulation & Control of Carbon Nanotube Formation

Sponsored by: Electronic, Magnetic & Photonic Materials Division, EMPMD-Nanomaterials Committee
Program Organizers: Jud Ready, Georgia Tech Research Institute - EOEML, Atlanta, GA 30332-0826 USA; Seung H. Kang, Agere Systems, Device and Module R&D, Allentown, PA 18109 USA; Lourdes G. Salamanca-Riba, University of Maryland, Materials Science and Engineering Department, College Park, MD 20742-2115 USA; Nagarajan Valanoor, Forschungzentrum Juelich, IFF and Institute for Electronic Materials, Juelich, Germany D52425

Monday PM Room: 3018
February 14, 2005 Location: Moscone West Convention Center

Session Chairs: Jud Ready, Georgia Tech, GTRI-EOEML, Atlanta, GA 30332-0826 USA; Seung H. Kang, Agere Systems, Allentown, PA 18109 USA; Lourdes G. Salamanca-Riba, University of Maryland, College Park, MD 20742-2115 USA

2:00 PM Opening Remarks

2:05 PM Invited
Designing Carbon-Based Nanotechnology on a Supercomputer: *David Tománek*[1]; [1]Michigan State University, Physics & Astron. Dept., E. Lansing, MI 48824-2320 USA

The continuous reduction of device sizes, which is rapidly approaching the atomic level, calls for new approaches to design and test future building blocks of Nanotechnology. Computer modeling is an indispensable tool to interpret phenomena associated with the nanometer scale. A plethora of unexpected phenomena is displayed by carbon nanostructures. Due to the stability of the sp^2 bond, carbon nanotubes are thermally and mechanically extremely stable and chemically inert. They contract rather than expand at high temperatures, and are the ultimate thermal conductors. At the same time, nanotubes may be tuned into ballistic electron conductors or semiconductors. sp^2 bonded nanostructures may change their shape globally by a sequence of Stone-Wales transformations. Specific nanotube assemblies may even acquire a permanent magnetic moment. In nanostructures that form during a hierarchical self-assembly process, even defects may play a different, often helpful role. Efficient self-healing processes may convert less stable atomic assemblies into other, more perfect structures, thus answering an important concern in molecular electronics. Defects may even be used in nano-scale engineering to form complex systems such as carbon foam or nanotube peapods. Unusual behavior is expected of devices based on nanotubes, including nonvolatile computer memory elements or nanoVelcro. In this presentation, I will show how some of these challenging problems can be most efficiently addressed in simulations on recently available massively parallel supercomputers.

2:35 PM Invited
Molecular Dynamics Study of Catalyzed Single-Walled Carbon Nanotube Nucleation: *Kim Bolton*[1]; Feng Ding[1]; Arne Rosen[1]; [1]Göteborg University and Chalmers University of Technology, Sch. of Physics & Engrg. Physics

Molecular dynamics simulations based on an empirical potential energy surface were used to study iron catalyzed nucleation and growth of narrow single-walled carbon nanotubes (SWNTs). The simulations show that small (ca. 1 nm) iron particles are in the liquid phase at experimental growth temperatures, and that SWNTs grow from these particles at temperatures between 800 and 1400 K. In contrast, at temperatures below 600 K graphene sheets encapsulate the particle, and above 1600 K a three-dimensional (3D) soot-like structure is formed. Nucleation of these carbon (C) structures can be divided into three stages: i) at short times all C atoms dissolve in the iron-carbide (FeC) particle, ii) at intermediate times the FeC cluster is highly supersaturated in C and carbon strings, polygons and small graphitic islands nucleate on the cluster surface, iii) at longer times the FeC cluster is supersaturated in C and a graphene sheet, SWNT or soot-like structure is grown. The simulation shows that the growing SWNT maintains an open end on the FeC cluster due to the strong bonding between the nanotube end atoms and the cluster. These strong interactions also yield SWNTs that have similar diameters to the FeC particles. The growth mechanism on larger particles, which can be in the solid phase under experimental conditions, is similar to that described above, although C atoms show only limited diffusion into the cluster before adding to the end of the growing SWNT.

3:05 PM Break

3:30 PM Invited
Controlled Geometry of Carbon Nanotubes: *Sungho Jin*[1]; [1]University of California, Dept. of Mechl. & Aeros. Engrg., 9500 Gilman Dr., La Jolla, CA 92093-0411 USA

By virtue of their exceptional electrical and mechanical properties, carbon nanotubes (CNTs) have been studied for many exciting, new applications such as electron field emitters, nano-scale manipulators, field-effect transistors, nano-interconnections, AFM probes, and bio or chemical interactions. In order to successfully utilize CNTs for such applications, the control of their size and morphology is essential. In this talk, various growth and microstructural controls of diameter, length, alignment, bending, and cutting of nanotubes will be discussed. Growth of patterned nanotubes or sharp nanocone arrays, multiple sharp bending of nanotubes for creation of zig-zag nanotubes, nano-scale shortening and opening of nanotubes, as well as coating or filling of nanotubes for nanocomposite formation will be described in relation to their potential applications.

4:00 PM Invited
Chirality Separation and Tuning the Electronic Structures of Carbon Nanotubes: *Young Hee Lee*[1]; [1]Sungkyunkwan University, Physics, Suwon, Kyungki 440-746 S. Korea

It is of crucial step to control the electronic structures of carbon nanotubes. The best way is of course to control the chirality during the synthesis, which is currently not available. One alternative is to separate nanotubes with specific chirality. We introduce gas adsorbates that lead to a selective etching of the nanotube edges. Among various types of simple gases, we found that it is only carbon dioxide that leads to a selective adsorption followed by a selective etching of zigzag nanotubes. We will introduce various approaches to choose either metallic or semiconductign nanotubes and propose a general strategy for chirality separation.

4:30 PM Invited
Growth and Properties of Carbon Nanotubes and Semiconducting Oxide Nanowires or Nanobelts: *A. M. Rao*[1]; [1]Clemson University, Dept. of Physics & Astron., Clemson, SC 29634 USA

One-dimensional nanostructures such as carbon nanotubes, semiconducting oxide nanowires or nanobelts exhibit unique fundamental properties that can be useful in several applications. I'll begin my talk by introducing a simple thermal CVD process in which doped nanotubes, and semiconducting oxide nanowires or nanobelts can be prepared in bulk quantities. Carbon nanotubes were prepared on bare quartz or oxidized silicon substrates using our thermal CVD process in which a liquid precursor, such as xylene, is used as the carbon source. Highly controlled doping of carbon nanotubes with nitrogen was accomplished by mixing appropriate amount of acetonitrile with xylene. The effect of nitrogen doping on the electronic and mechanical properties of carbon nanotubes will be presented. In addition to the synthesis and doping of carbon nanotube, nanowires and nanobelts of oxides, sulfides and nitrides of low melting metals such as gallium, indium and tin were also prepared using our CVD system. These nanostructures were synthesized using metal films and corresponding reactant gases at ambient pressure in a catalyst-free environment. Some of the fundamental properties of these nanostructures monitored using Raman spectroscopy, SEM, high resolution TEM, and vibrating reed measurements will be presented.

5:00 PM Invited
Carbon Nanotubes and Silicon Nanowires: *Z. F. Ren*[1]; [1]Boston College, Dept. of Physics, Chestnut Hill, MA USA

The carbon nanotubes aligned periodically have many potential applications in electronics, optics, etc. In this talk, I will discuss the aligned carbon nanotubes grown by plasma enhanced hot filament chemical vapor deposition on Ni films by magnetron sputtering, Ni dots by e-beam lithography, Ni dots by electrochemical deposition, and two-dimensional periodical nickel dot array by nanosphere self-assembly. The size of the nickel dot and spacing between them and location are tunable by the preparation methods. Two new techniques were developed to make triangular Ni dots and aligned carbon nanotubes. With these arrays, a variety of applications have been studied includ-

ing field emission, nanoelectrode, photonic band gap crystals, etc. In addition, I will talk about our recent studies on synthesis of silicon nanowires.

5:30 PM
Alignment of Carbon Nanotubes via Electrically Biased Thermal Filament Chemical Vapor Deposition: *Stephan Parker Turano*[1]; [1]Georgia Tech Research Institute, 925 Dalney St., Baker Rm. 114, Atlanta, GA 30332 USA

The focus of this research is to synthesize aligned carbon nanotubes (CNTs) on silicon substrates using transition metal catalysts such as Fe and Ni. CNTs are synthesized using thermal chemical vapor deposition (CVD) with temperature ranging between 700 and 900°C. In addition, an electric field was created in the deposition chamber using tungsten filaments under an electric bias. Results show that a significant amount of nanotube alignment occurs during the synthesis process. Coiled nanotubes, and nanotubes which exhibit perfect 90° bends, are also present in samples which are subjected to an electric field. This work suggests that CNT orientation can be controlled during synthesis and that CNTs may eventually be synthesized directly into electronic circuits or other devices.

Arsenic Metallurgy: Fundamentals & Applications: Removal of Arsenic and its Precipitation from Process Streams I

Sponsored by: Extraction & Processing Division, EPD-Copper, Nickel, Cobalt Committee, EPD-Process Fundamentals Committee, EPD-Pyrometallurgy Committee, LMD/EPD-Recycling Committee
Program Organizers: Ramana G. Reddy, University of Alabama, Department of Metals and Materials Engineering, Tuscaloosa, AL 35487-0202 USA; V. Ram Ramachandran, Scottsdale, AZ 85262-1352 USA

Monday PM Room: 2014
February 14, 2005 Location: Moscone West Convention Center

Session Chairs: George P. Demopoulos, McGill University, Metals & Matls. Engrg., Montreal, Quebec H3A 2B2 Canada; Tina Maniatis, Applied Biosciences, Salt Lake City, UT 84152 USA

2:00 PM
Arsenic Removal from Mine and Process Waters by Lime/Phosphate Precipitation: *Larry G. Twidwell*[1]; Jay McCloskey[2]; Michelle Gale Lee[3]; Jennifer Saran[4]; [1]Montana Tech of University of Montana, Sch. of Mines & Engrg., 1300 W. Park St., Butte, MT 59701 USA; [2]MSE-Technology Applications, Process Engrg., 200 Technology Way, Butte, MT 59701 USA; [3]MSE-Technology Applications, QA, 200 Technology Way, Butte, MT 59701 USA; [4]Kennecott Copper, Salt Lake City, UT 84044 USA

The removal of dissolved arsenic from mine wastewaters utilizing a lime/phosphate precipitation technique has been studied on a laboratory scale at Montana Tech of The University of Montana and on a pilot scale at MSE-Technologies Applications as a wastewater treatment process potentially capable of removing dissolved arsenic to <10 ug/L. Arsenic bearing lime and lime/phosphate slurries were subjected to laboratory extended time air-sparged aging for over four years. The lime slurries released their arsenic back into solution in a relatively short period of time, whereas the lime/phosphate slurries showed limited redissolution of arsenic. The developed process has been pilot scale tested by MSE-TA for the EPA Mine Waste Technology Program on two waters, ASARCO smelter blowdown water and Mineral Hill groundwater. The laboratory study results will be presented and discussed in this presentation. The pilot scale results will be presented and discussed in a companion presentation.

2:25 PM
Arsenic Removal from Mine and Process Waters by Lime/Phosphate Precipitation: Pilot Scale Demonstration: *Jay McCloskey*[1]; Michelle Gale Lee[1]; Larry G. Twidwell[2]; [1]MSE Technology Applications, Process Engrg., 200 Tech. Way, Butte, MT 59701 USA; [2]Montana Tech of University of Montana, Sch. of Mines & Engrg., 1300 W. Park St., Butte, MT 59701 USA

The removal of dissolved arsenic from mine wastewaters utilizing a lime/phosphate precipitation technique has been studied on a laboratory scale at Montana Tech of The University of Montana and on a pilot scale at MSE-Technology Applications as a wastewater treatment process potentially capable of removing dissolved arsenic to <10 ug/L. The developed process has been pilot scale tested by MSE-TA for the EPA Mine Waste Technology Program on two waters, ASARCO smelter blowdown water and Mineral Hill groundwater. Two other technologies were evaluated at the same time for comparison, e.g., alumina adsorption and ferrihydrite adsorption. The pilot scale results will be presented and discussed in this presentation. The background laboratory studies are presented in a companion presentation.

2:50 PM
Meeting Arsenic Standards in Drinking Water by January 2006: A Review of Available Technologies: *V. Ram Ramachandran*[1]; Ramesh Narasimhan[2]; [1]Consulting Engineer, 9650 E. Peregrine Place, Scottsdale, AZ 85262 USA; [2]Narasimhan Consulting Services, 3150 N. 24th St., Ste. D-104, Phoenix, AZ 85016 USA

Arsenic occurs naturally in rocks and soil, water, air, plants and animals. It can be further released into the environment through natural activities such as volcanic action, erosion of rocks and through human actions. Higher levels of arsenic tend to be found more in ground water sources than in surface water sources of drinking water. Compared to the rest of USA, western states have more systems with arsenic levels greter than 10 parts per billion(ppb). The US Environmental Protection Agency(EPA) has historically regulated arsenic in drinking water at 50 ppb, but the agency will lower the maximum contaminant level(MCL) for arsenic to 10 ppb by January 2006. This paper reviews briefly a)arsenic chemistry and removal mechanisms and b)the available treatment processes to attain the drinking water standard of 10 ppb by 2006. The combining of an appropriate removal method with an existing system depends on several factors such as nature of arsenic, the water source, existing plant equipment and processess, site conditions etc. The paper also includes one or two case studies from the State of Arizona.

3:15 PM
Coprecipitation of Arsenic with Fe(III), Al(III) and Mixtures of Both in a Chloride System: Robert G. Robins[1]; *Pritam Singh*[1]; Radhanath P. Das[2]; [1]Murdoch University, Div. of Sci. & Engrg./Chmst. Dept., Murdoch, WA 6150 Australia; [2]Regional Research Laboratory, CSIR/Dept. of Hydrometall., Bhubaneswar, Orissa 751013 India

The removal of arsenic from hydrometallurgical process and effluent streams and also from drinking water, has among other methods, utilised chemical coprecipitation with Fe(III) and Al(III) for many decades. It is considered that As(V) is the oxidation state that is most efficiently removed by chemical coprecipitation. The literature reports many studies in which an aqueous solution of either Fe(III) or Al(III) was the reagent that had been investigated for coprecipitation of As(V). There is argument as to whether Fe(III) or Al(III),used separately, is the most effective reagent for coprecipitation, and also concerning the optimal M(III):As(V) ratio for best removal. Many misconceptions have evolved from published work and this paper will address some of those and present experimental compari sons in evidence, More importantly we report the superior results from using a mixed Fe(III)-Al(III) reagent for coprecipitation of As(V), rather than the individual Fe(III) or Al(III) solutions separately.

3:40 PM Break

3:55 PM
The Effect of Silicate on the Adsorption of Arsenate on Co-Precipitated Ferrihydrite: *Pritam Singh*[1]; Wensheng Zhang[1]; David M. Muir[2]; Robert G. Robins[1]; [1]Murdoch University, Div. of Sci. & Engrg./Chmst. Dept., Murdoch, Western Australia 6150 Australia; [2]CSIRO Minerals, PO Box 90, Bentley, Western Australia 6982 Australia

Dissolved silicate interferes with the removal of As(V) from aqueous solutions by co-precipitation/adsorption on ferrihydrite. It causes an increase in the residual As(V) and Fe(III) in solution. The effect is a function of initial silicate concentration and pH of the solution from which co-precipitation/adsorption occurs. In the presence of silicate, the residual As(V) in water increases rapidly at pH>5. For a solution with initial 1 mg/L As and 30 mg/L Fe(III), when silicate is doubled from 20 to 40 mg/L, the coprecipitation/adsorption of As(V) on ferrihydrite at pH 7 results in five times higher residual As(V) (0.05 to 0.28 mg/L). At the same time, the residual Fe(III) in solution is doubled (approximately 4 to 8 mg/L). It is proposed that the silicate effect is due to a combination of complexation reactions between Fe(III), Si(IV) and As(V) species, and competition between As(V) and Si(IV) for adsorption sites on ferrihydrite.

4:20 PM
Coprecipitation of As(V) with Fe(III) in Sulfate Media: Solubility and Speciation of Arsenic: *Yongfeng Jia*[1]; Ning Chen[2]; George P. Demopoulos[1]; [1]McGill University, Dept. of Mining, Metals & Matls. Engrg., 3610 Univ. St., Montreal, Quebec H3A 2B2 Canada; [2]Canadian

Light Source Inc., University of Saskatchewan, 101 Perimeter Rd., Saskatoon, SK S7N 0X4 Canada

Lime neutralization and co-precipitation of As(V) with iron(III) is the best and most economical method for the removal of arsenic from mineral processing solutions and effluents. However, the arsenate fixation mechanism in the coprecipitated solid is not fully understood. It was suggested by some researchers to be a ferrihydrite precipitation process during which arsenate is removed by adsorption on ferrihydrite. In this study, XRD, EXAFS and microprobe were employed for the speciation of arsenic and the effect of various factors were also investigated. The results indicate that the coprecipitation is a more complicated process than simple adsorption. Poorly crystalline ferric arsenate was observed for the first time to be present in the coprecipitated solid. In case lime as base, there exists some type of Ca-Fe-arsenate association. A general term "coprecipitate" is suggested to describe the precipitated arsenic-bearing solid instead of those widely used specific terms "arsenical ferrihydrite" or "arsenic-bearing ferrihydrite".

4:45 PM
Arsenic in Yellowknife, NWT, Canada: *W. R. Cullen*[1]; K. J. Reimer[2]; C. Ollson[3]; [1]University of British Columbia, Chmst. Dept., Vancouver, BC Canada; [2]Royal Military College of Canada, Environmental Scis. Grp., Kingston, Ontario Canada; [3]Jacques Whitford Environmental Limited, Ottawa, Ontario Canada

The Giant Mine began gold production in Yellowknife, Northwest Territories, Canada, in 1948. Soon after this is was decided to store the arsenic trioxide dust from the smelter underground. The current situation is that the mine has now ceased operations leaving 260,000 tons of 78% by weight arsenic trioxide dust stored in 15 underground chambers. The first part of the talk will outline the management options that include leaving the dust in place or removing it to the surface where further processing or stabilizing would be required. The processing of gold ore at both mines – the Giant and Con – in Yellowknife has resulted in tailings ponds and surface soils containing high concentrations of arsenic. This has added to a naturally elevated arsenic concentration in the area. Closure plans require the development of practical and cost-effective ways of mitigating the environmental impact of this contamination. The first step in such a process is to identify the actual environmental and human health risks. The second talk will describe the use of laboratory techniques (gastric fluid extraction) that simulate exposure scenarios. The results of these studies suggest that the risk is much less than would have otherwise been expected and could form the basis of remediation plans costing much less than would otherwise be the case.

Beta Titanium Alloys of the 00's: Applications II

Sponsored by: Structural Materials Division, SMD-Titanium Committee
Program Organizers: Rod R. Boyer, Boeing Company, Metall./6-20J1, Seattle, WA 98124-2207 USA; Robert F. Denkenberger, Ladish Co., Inc., Cudahy, WI 53110-8902 USA; John C. Fanning, TIMET, Henderson, NV 89009 USA; Henry J. Rack, Clemson University, School of Materials Science & Engineering, Clemson, SC 29634-0921 USA

Monday PM Room: Salon 10/11
February 14, 2005 Location: San Francisco Marriott

Session Chairs: Rodney R. Boyer, Boeing Company, Metall./6-20J1, Seattle, WA 98124 USA; K. O. Yu, RMI Titanium Company, Niles, OH 44446-0269 USA

2:00 PM
Recent Developments in Beta Strip Alloys: *John C. Fanning*[1]; [1]TIMET, PO Box 2128, Henderson, NV 89009 USA

The strip-producibility, good fabricability and excellent mechanical properties of beta alloys make them useful for a variety of fabricated sheet metal structures on airframes and aeroengines. In particular, TIMETAL 15-3 is used for ECS (Environmental Control System) ducting on the Boeing 777 and Airbus A380. For applications that require exposure to higher temperatures, such as the plug&nozzle assemblies on various civil and military aircraft, TIMETAL 21S is now widely used. This paper will summarize recent developments in the properties and processing of these alloys with regards to aerospace and other applications.

2:30 PM
Properties and Processing of TIMETAL® LCB: *Yoji Kosaka*[1]; Stephen P. Fox[1]; Kurt Faller[2]; Steven H. Reichman[2]; [1]TIMET, Henderson Techl. Lab., PO Box 2128, Henderson, NV 89009 USA; [2]TIMET Automotive, 900 Hemlock Rd., Morgantown, PA 19543 USA

TIMETAL® LCB was introduced more than 10 years ago targeting automotive suspension spring applications. The alloy development aim was to use a low cost formulation by selecting less expensive raw materials than typical beta titanium alloys. Following the first successful application of TIMETAL® LCB suspension springs to series production vehicles, the 2000 Volkswagen Lupo FSI, the springs have been used for Ferrari Challenge Stradale since 2003. The most recent development effort has been focused on the generation of metallurgical and mechanical service data of the alloy, and the establishment of low cost processing of coils and bars. This paper will introduce various properties of TIMETAL® LCB products that can be useful in the design and the consideration of spring applications. Recent progress in the processing of TIMETAL®LCB will also be introduced and discussed.

2:55 PM
Candidate Materials for Aerospace and Automotive High Strength Fastener Applications: *James G. Ferrero*[1]; [1]Perryman Company, 213 Vandale Dr., Houston, PA 15342 USA

There are many commercially available titanium alloys that have exhibited the capability of achieving high strengths. Many of these alloys have not been seriously considered for fastener applications due to their cost or availability as coil or bar. However, as new designs, increased material requirements and larger aircraft are being built the need to reduce weight and improve performance continues to be a major issue. The possibility of reducing weight by replacing currently used steel fasteners in various sizes is a great incentive. Over the past few years, many of these alloys have been processed to bar and coil product to evaluate there capabilities as potential fastener materials. This paper will review and summarize the mechanical properties, tensile, shear, notch tensile and available fatigue, as well as the microstructure of these candidate alloys.

3:25 PM Break

3:40 PM
Ti-200: A Titanium Alloy Developed for 200 ksi (1380 MPa) Applications: *Paul Bania*[1]; [1]TiPro LLC, 1011 Industrial Rd., Ste. #5, Boulder City, NV 89005 USA

A new titanium alloy has been developed by Ti-Pro LLC - designated "Ti-200" - for applications requiring tensile strengths at or above 200 ksi (1380 MPa). This paper will review the experimental studies leading to the final chemistry selection as well as some preliminary properties of the new alloy. Applications for the alloy include various small forgings/machined parts for automotive racing applications as well as high strength titanium fasteners.

4:05 PM
Mechanical Properties of Beta Processed Ti-17: *Andy Woodfield*[1]; [1]General Electric Aircraft Engines, Neumann Way, MD M-89, Cincinnati, OH 45215 USA

Abstract not available.

4:35 PM
Microstructure-Properties of Beta Titanium Alloy Castings: *E. Y. Chen*[1]; D. R. Bice[1]; [1]TiTech International, Inc., PO Box 3060, Pomona, CA 91769-3060 USA

The number of applications of titanium castings has expanded greatly in the last decade due to factors such as improved casting quality and mechanical properties as well as better shape-making capabilities. The bulk of the titanium casting manufactured has remained Ti-6Al-4V, Ti-6Al-2Sn-4Zr-2Mo, and CP-Ti. Beta titanium alloys have been widely used as forgings, but much less so as castings despite the potential benefits. This study investigates the castability and microstructure-properties of several beta and alpha + beta titanium alloys including Ti-10V-2Fe-3Al and Ti-15V-3Al-3Cr-3Sn. A comparison of the mechanical properties of the beta castings versus those of their forged counterparts will also be made.

Biological Materials Science and Engineering: Biological Materials II

Sponsored by: Structural Materials Division, Electronic, Magnetic & Photonic Materials Division, Society for Biomaterials, Surfaces in Biomaterials Foundation, SMD-Mechanical Behavior of Materials-(Jt. ASM-MSCTS), EMPMD/SMD-Biomaterials Committee
Program Organizers: Marc Andre Meyers, University of California, Department of Mechanical and Aerospace Engineering, La Jolla, CA 92093-0411 USA; Sungho Jin, University of California, Department of Materials Science, La Jolla, CA 92093 USA; Roger J. Narayan, Georgia Tech, School of Materials Science and Engineering, Atlanta, GA 30332-0245 USA

Monday PM Room: 3009
February 14, 2005 Location: Moscone West Convention Center

Session Chairs: George Mayer, University of Washington, Dept. of Matls. Sci. & Engrg., Seattle, Washington USA; A. G. Evans, University of California, Matls. Dept., Santa Barbara, CA 93106-5050 USA

2:00 PM Invited
Mechanisms Governing the Inelastic Deformation of Bone: *A. G. Evans*[1]; C. Mercer[1]; P. Hansma[1]; M. He[2]; [1]University of California, Santa Barbara, CA USA

To understand the inelastic response of cortical and trabecular bone, a three-part investigation has been conducted. In the first, a flexural test protocol has been designed and implemented that monitors the axial and transverse strains on both the tensile and compressive surfaces of cortical bone. The results are used to assess the relative contributions of dilatation and shear to the inelastic deformation. A deconvolution has been used to affirm that the stress/strain curves in tension and compression are consistent with results in the literature. Unload/reload tests have characterized the hysteresis and provided insight about the mechanisms causing the strain. In the second part, a constitutive law representative of the deformation is selected. To demonstrate consistency, it is first used to reconstruct the flexural response. Thereafter, it is implemented to illustrate the coupled buckling and bending of ligaments that occurs in osteoarthritic trabecular bone loaded in compression. Stress/strain curves are calculated and shown to be consistent with measurements reported in the literature. The third part devises a model for the intrinsic stress/strain response of bone, based on a recent assessment of the nano-scale organization of the collagen fibrils and mineral platelets. The model is used to rationalize the inelastic deformation in tension, as well as the permanent strain and the hysteresis.

2:30 PM Invited
Growth, Structure, and Mechanical Response of Abalone Shells: *Marc Andre Meyers*[1]; Albert Lin[1]; Julie Muyco[1]; [1]University of California, Matls. Sci. Prog., La Jolla 92093-0411 USA

The growth of the nacreous layers (aragonite) was observed by inserting glass plates in the extrapallial layer for different time periods, removing them, and observing them by scanning electron microscopy. Details of the growth sequence were revealed. The mechanical properties and structure of mineral and organic phases was characterized by nanoindentation and atomic force microscopy.Individual protein chains were identified in the nanoorganic (~25 nm thick)layer between the aragonite tiles. This layer presented holes with a diameter of approximately 40 nm. Quasi-static compression and three-point bending tests were carried out. The mechanical response of the abalone is correlated with the microstructure and damage mechanisms. The mechanical response is found to vary significantly from specimen to specimen and requires the application of Weibull statistics in order to be quantitatively evaluated. The abalone exhibited orientation dependence of strength: the compressive strength when loaded perpendicular to the shell surface was approximately 50% higher than parallel to the shell surface. The compressive strength of abalone is 1.5 - 3 times the tensile strength (as determined from flexural tests), in contrast with monolithic ceramics, for which the compressive strength is typically an order of magnitude greater than the tensile strength. Quasi-static compressive failure in both shells occurred gradually, in a mode described as “graceful failure”. The shear strength of the organic/ceramic interfaces was determined by means of a shear test and was found to be approximately 30 MPa. Considerable inelastic deformation of these layers (up to a shear strain of 0.4) preceded failure. The mechanical response of the organic nanolayers and mesolayers (growth bands) determines the high tensile strength of the shell and its associated high toughness. Crack deflection, delocalization of damage, plastic microbuckling (kinking), and viscoplastic deformation of the organic layers are the most important mechanisms contributing to the unique mechanical properties of these shells.

3:00 PM Invited
Biomimetic Mineralization of Printed Polymer Gels: *Paul Calvert*[1]; [1]University of Massachusetts, Dept. of Textile Scis., N. Dartmouth, MA 02747 USA

The factors controlling biomineralization are not well understood in most cases. Nucleation on organic surfaces is believed to be important in some cases, in others nucleation occurs within a gel. Inhibitors are present which may control the crystal morphology or totally prevent growth. In some cases mineralization seems to arise from a localized source of the inorganic ions. In this work we have explored the role of immobilized enzymes in promoting mineralization of polymer gels. Printing methods were used to deposit gels with thicknesses from less than one micron up to hundreds of microns. We show that heavily mineralized gels can be formed in this way if they are thick enough that precipitation predominates over outward diffusion of the ions. The role of the gel matrix material in the process will also be discussed.

3:30 PM Break

3:45 PM Invited
Nanomechanical Characterization of Nanoscale Biomaterials: *Chwee Teck Lim*[1]; [1]National University of Singapore, Bioengrg. & Mechl. Engrg., 9 Engrg. Dr. 1, Singapore 117576

Much interest has been generated recently in the use of nanostructured biomaterials for tissue engineering so as to create biological alternatives for implants. Biodegradable polymers in the form of highly porous nanofibrous scaffolds are ideal in accommodating cells and guiding their growth for tissue regeneration in three dimensions. Besides biocompatibility, suitable porosity and sufficient surface area for cell attachment, these polymeric scaffolds should also have the structural integrity and mechanical strength to maintain the desired shape before the new tissue takes over. In fact, studies have shown that the mechanical constraints imposed on cells seeded in scaffolds can affect cell growth, migration and differentiation. Therefore, there is a need to study the structural and nanomechanical properties of individual nanofibers that make up the entire scaffold. However, due to the difficulty in isolating and manipulating individual nanofibers and measuring the very small force and deformation involved, little work has been done in this area. This talk will highlight some of the challenges as well as innovative experimental techniques that we have developed in our research group to investigate the nanomechanical properties of these nanoscale biomaterials.

4:05 PM
Dynamic Fracture of Bovine Cortical Bone: A Systematic Study of Strain Rate Effects: *Raghavendra R. Adharapurapu*[1]; Kenneth S. Vecchio[1]; Fengchun Jiang[1]; [1]University of California, Dept. of MAE, Matls. Sci. & Engrg. Grp., 9500 Gilman Dr., MC-0411, La Jolla, CA 92093-0411 USA

True clinical fracture of bones in bovine, race horses or humans occur predominantly during impact loading (for e.g. car accidents, falls or physical violence). Although, static fracture tests provide an estimate of fracture toughness or R-curve behavior in bones, the static toughness values may be ill suited for predicting failure under dynamic loading conditions due to the visco-elastic response of bone (i.e. strain rate dependent properties). Despite decades of the study on deformation rate dependency of cortical bone properties such as compression and fracture toughness, high quality dynamic fracture toughness data remains limited. Preliminary tests (compression and fracture toughness) have been conducted on dry and wet bovine cortical bone under both static and dynamic loading conditions with loading parallel and perpendicular to the bone axis (longitudinal and transverse respectively). The strain rate in compression tests varied between 10^{-3} to $10^{3}s^{-1}$, and the stress intensity rate varied between 10^{-3} to 10^{6} MPa-√m/s. While low strain rate tests were conducted on conventional mechanical testing machines, high strain rate experiments were conducted on a split-Hopkinson bar under compression and a novel three-point bend configuration. The influence of wetting agent on the failure properties was also investigated by testing bone exposed to a salt solution or acetone for different periods. The fracture morphology and the extent of microcracking of bone in each case were characterized using SEM, and an attempt is made to relate it to the rate dependency of fracture toughness of the cortical bone. Interpretation of the fracture mechanisms is conducted in terms of structural attributes of bone, such as the composite nature of bone with hierarchical structure

over different length scales that produce strong materials from weak constituents. It is believed that such understanding is crucial for mechanistic interpretation of cortical bone fracture phenomenon and eventually for predicting bone failure reliably.

4:25 PM
Creation of Nanostructured Hydroxyapatite (Synthetic Bone) by Hydrothermal Conversion of Seashells: *Kenneth S. Vecchio*[1]; Xing Zhang[1]; [1]University of California, Dept. of MAE, Matls. Sci. Grp., 9500 Gilman Dr., MC-0411, La Jolla, CA 92093-0411 USA

Hydroxyapatite is a bioactive material and the main component of human bone. Due to its biocompatibility and osteoconductive properties, it has many applications, such as bone graft substitutes, sustained-release drug delivery devices, purification of proteins, etc. Many of these medical implant applications require highly densified implants with mechanical strength high enough for load bearing. The major hurdle to synthesis of synthetic bone from calcite is the difficulty of making dense forms of hydroxyapatite, structured in a manner that impart good mechanical properties. On the other hand, shells and marine bones, which are composed of aragonite/calcite crystals, have dense, tailored structures that impart excellent mechanical properties to these structures. Seashells, such as conch, clams, and abalone, have hierarchical and optimally designed architectures with similar mechanical properties as hard bone. We have recently developed a way to convert the aragonite/calcite crystals within the shell to hydroxyapatite crystals, making the possibility of dense, well-structured, synthetic bone a realizable goal. This project is focusing on optimizing the hydrothermal conversion process to convert the aragonite/calcite to hydroxyapatite, while maintaining the architecture of the shell and marine bone structures. The applications for such synthetic bones include dental implants, biocompatible prosthetic interfaces, bone replacements and many other medical implants.

4:45 PM
Phase Transformation of the Nano-Sized Hydroxyapatite Synthesized by Hydrolysis Using In-Situ High Temperature X-Ray Diffraction: *Wei-Jen Shih*[1]; Jian-Wen Wang[2]; Moo-Chin Wang[3]; Min-Hsiung Hon[1]; [1]National Cheng Kung University, Dept. of Matls. Sci. & Engrg., 1 Ta-Hsueh Rd., Tainan 70101 Taiwan; [2]Chung Hwa College of Medical Technology, Dept. of Environml. & Safety Engrg., 89 Wen-Hua 1st St., Rende Shiang, Tainan 71703 Taiwan; [3]National United University, Dept. of Matls. Sci. & Engrg., 1 Lien-Da, Kung-Ching Li, Miao Li 360 Taiwan

The biodegradable hydroxyapatite (HA) was synthesized by hydrolysis and characterized using high temperature X-ray diffraction (HT-XRD), differantial thermal analysis (DTA), thermogravimetry (TG), scanning electron microscopy (SEM), and FT-IR spectrometer. The in-situ phase transformation of nano-sized HA synthesized from $CaHPO_4$¡E$2H_2O$ (DCPD) and $CaCO_3$ with a Ca/P=1.5 in 2.5 M $NaOH_{(aq)}$ at 75°C for 1 h was investigated by HT-XRD from RT to 1500°C. The synthetic HA recrystallized at 600°C and maintained as the major phase until 1400°C. The HA steadily transformed to α-tricalcium phosphate α-TCP) and at 1500°C α-TCP became the major phosphate phase. The minor CaO phase appears at the temperature of 750°C due to the decomposition of CaCO3 and vanished at 1300°C. The Na^+ impurity from the hydrolysis process was responsible for the formation of $NaCaPO_4$ phase, appearing above 700°C and disappeared at 1300°C.

5:05 PM
Nucleation, Growth, Characterization and Biocompatibility of Biomimetic Apatite Layers Formed on Titanium Alloy: K. C. Baker[2]; M. A. Anderson[1]; S. A. Oehlke[1]; A. I. Aastachkina[2]; D. C. Haikio[2]; *J. Drelich*[1]; S. W. Donahue[2]; N. S. Istephanous[3]; [1]Michigan Tech, Matls. Sci. & Engrg., 1400 Townsend Dr., Houghton, MI 49931 USA; [2]Michigan Tech, Biomed. Engrg., Houghton, MI USA; [3]Medtronic USA, Inc., Matls. & Bioscis. Ctr., 710 Medtronic Pkwy., Minneapolis, MN 55432 USA

This study focuses on the growth, characterization and biocompatibility of bone-like apatite layers on Ti-6Al-4V alloy produced through diminished time duration chemical immersion. The method presented combines a pre-calcification step, in which samples were immersed in a boiling Ca(OH)2 solution to initiate and increase ion exchange. Subsequent immersion in a supersaturated calcium-phosphate solution (SCPS) produced homogenous coatings with thicknesses of 15-20 microns, 100% coverage and crystal sizes of 1-2 microns in as little as 4 days. Coated samples were favored biologically over non-coated samples by cultured osteoblast cells as evidenced through alkaline phosphatase activity assays. This study asserts that an industrially viable method of chemical immersion in a SCPS, coupled with simple pre-treatments can produce apatite coatings that favor positive biological interactions, conducive to osseointegration.

5:25 PM
A Biomimetic Approach to the Deposition of Zirconia Films on Self-Assembled Nanoscale Templates: *Junghyun Cho*[1]; [1]SUNY Binghamton, Mechl. Engrg., T. J. Watson Sch. of Engrg., PO Box 6000, Binghamton, NY 13902-6000 USA

A biomimetic synthesis technique is employed to deposit ceramic films on nanoscale organic materials. Specifically, phosphonate-based self-assembled monolayers (SAM) are used as the organic template, onto which a ZrO_2 film is grown in situ in an aqueous solution at near room temperature (≈80°C). This process mimics biomineralization involving the controlled nucleation and growth of the inorganic (ceramic) materials. It is shown that surface functionality of the SAM plays a crucial role by: i) providing surface nucleation sites for the covalently-bonded ceramic film, and ii) promoting electrostatic attraction between the SAM surface and the colloidal clusters or particles precipitated in the solution. The resultant zirconia films consist of sub-micron sized particles that are formed by an enhanced hydrolysis of zirconium sulfate. The mechanisms of film formation are systematically studied by tailoring the film structure from solution chemistry and SAM functionalities. In particular, the cross-sectional TEM work is performed to quantitatively analyze the film structure as well as interfacial region of the biomimetic ceramic films. Further, the integrated nanoindentation/AFM technique is extensively used to characterize the mechanical properties of the films. This growth mechanism is sufficiently general that it may be applicable to other oxide systems. Therefore, the ultimate goal of this study is to develop a process that can yield dense, solid ceramic structure with enhanced properties.

Bulk Metallic Glasses: Processing and Fabrication II

Sponsored by: Structural Materials Division, SMD-Mechanical Behavior of Materials-(Jt. ASM-MSCTS)
Program Organizers: Peter K. Liaw, University of Tennessee, Materials Science and Engineering, Knoxville, TN 37996-2200 USA; Raymond A. Buchanan, University of Tennessee, Materials Science and Engineering, Knoxville, TN 37996-2200 USA

Monday PM — Room: 3006
February 14, 2005 — Location: Moscone West Convention Center

Session Chairs: Todd C. Hufnagel, Johns Hopkins University, Matls. Sci. & Engrg., Baltimore, MD 21218 USA; Robert W. Hyers, University of Massachusetts, Mechl. Engrg., Amherst, MA 01003 USA

2:00 PM
Anomalous Thermal Expansion in Undercooled Liquid Ti39.5Zr39.5Ni21: *Richard C. Bradshaw*[1]; Robert W. Hyers[1]; Jan R. Rogers[2]; Tom J. Rathz[2]; Geun W. Lee[3]; Anup K. Gangopadhyay[3]; Ken F. Kelton[3]; [1]University of Massachusetts, Mechl. Engrg. Dept., 160 Governors Rd., Elab 220, Amherst, MA 01003 USA; [2]NASA, Marshall Space Flight Ctr., MC SD46, NASA MSFC, Huntsville, AL 35812 USA; [2]University of Alabama, Ctr. for Automation & Robotics, Huntsville, AL 35899 USA; [3]Washington University, Dept. of Physics, St. Louis, MO 63130 USA

Quasicrystal alloys show great promise in the areas of low friction coatings, electronic applications and hydrogen storage. Discovered in 1984, the properties and behaviors of quasicrystals are still under study. Particular emphasis is being placed on the study of thermophysical properties in the undercooled liquid regime. The icosahedral ordering in the undercooled liquid is similar to the quasicrystal structure; the degree of ordering in the undercooled liquid should be reflected in changes in thermophysical properties. A non-linearity in thermal expansion has been observed in the undercooled liquid state in a Ti39.5Zr39.5Ni21 quasicrystal forming alloy. This non-linearity correlates with anomalous behavior in surface tension and specific heat as well as x-ray structure factor. Non-contact processing and optical measurement techniques allow access to the undercooled liquid. An overview of the processing and measurement technique is presented with the thermal expansion measurements.

2:20 PM
Short-Range Order Studies in Aero-Acoustic Levitation Processed Zr-Based Bulk Amorphous Alloy: *James J. Wall*[1]; J. K.

Richard Weber[2]; Peter K. Liaw[1]; Hahn Choo[1]; [1]University of Tennessee, Dept. of Matls. Sci. & Engrg., Knoxville, TN 37996 USA; [2]Containerless Research, Inc., Evanston, IL 60201 USA

Aero-acoustic levitation, was used to fabricate Zr57Ti5Ni8Cu20Al10 bulk metallic-glass at cooling rates of 2, 5, 10, 20, 100, and 300 K/s. In-situ levitation-calorimetry during processing showed the evidence of increasing the exothermic activity in the samples with decreasing cooling rate, suggesting an evolution of short-range order at the lower cooling rates. To investigate this phenomenon, neutron scattering experiments were performed on the ex-situ samples. Pair-distribution-function analyses showed that the atomic structure of the samples processed at a lower cooling rate exhibited a tendency to form more densely packed short-range atomic clusters. It is suggested that this behavior acted to lower the specific enthalpy of the specimens, enhancing the thermodynamic stability. This work is supported by the NSF International Materials Institutes Program DMR-0231320, with Dr. Carmen Huber as the program director.

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Exploration of Bulk Aluminum Glass: *James Michael Scott*[1]; Wynn S. Sanders[2]; Daniel B. Miracle[2]; Scott D. Bohnenstiehl[2]; Jenifer S. Warner[2]; [1]UES, Inc., 4401 Dayton-Xenia Dr., Dayton, OH 45432 USA; [2]Air Force Research Laboratory, Matl. & Mfg. Direct., 2230 Tenth St., Wright-Patterson AFB, OH 45433 USA

Previous research has led to a new strategy for the prediction of new bulk metallic glasses. This strategy includes: application of a unique topological relationship via atomic size distribution plots, preferred radius ratios that enable efficient atomic packing, appropriate alloying element selection to depress the liquidus relative to the glass transition temperature and new structural modeling concepts. In addition, a wedge casting technique offers a simple method for alloy evaluation and gives an effective ranking of relative glass forming ability. Composition space of ternary marginal glass formers has been systematically explored via the addition of quaternary and higher order alloying elements based upon this strategy and use of this wedge casting technique. The results obtained from this systematic search will be presented and discussed.

3:00 PM

A Calphad Approach for Predicting the Bulk Glass-Forming Tendency of Zr-Ti-Ni-Cu-Al Alloys: *Hongbo Cao*[1]; Dong Ma[1]; Y. Austin Chang[1]; Ling Ding[1]; Ker-Chang Hsieh[2]; [1]University of Wisconsin, Matls. Sci. & Engrg., 1509 Univ. Ave., Madison, WI 53706 USA; [2]Sun Yat Sen University, Inst. of Matls. Sci. & Engrg., Kaohsiung Taiwan

A Calphad approach has been used to predict the compositions of Zr-Ti-Cu-Ni-Al alloys exhibiting low-lying-liquidus surfaces, which tend to favor the formation of bulk metallic glasses. The idea is to build on all thermodynamic information from the lower order constituent binaries and ternaries to obtain the thermodynamic properties of the higher order alloys. These thermodynamic properties enable us to predict those alloy compositions with low-lying-liquidus surfaces. The predicted alloy compositions of this quinary system for glass formation agree well with those determined experimentally. Using these calculations as a guide we identified a series of new alloys, which can be readily cast into glassy rods of 10 mm in diameter.

3:20 PM Break

3:40 PM

Producing Amorphous Joints in Metallic Glasses by Reactive Joining: *Jonathan C. Trenkle*[1]; Jiaping Wang[1]; Omar M. Knio[2]; Etienne Besnoin[2]; Tim P. Weihs[2]; Todd C. Hufnagel[1]; [1]Johns Hopkins University, Matls. Sci. & Engrg., 102 Maryland Hall, 3400 N. Charles St., Baltimore, MD 21218 USA; [2]Reactive NanoTechnologies, 111 Lake Front Dr., Hunt Valley, MD 21030 USA

Reactive multilayer foils are comprised of nanoscale layers of materials that can sustain a self-propagating exothermic reaction. Al/Ni foils can be used to join metallic glasses with no evidence of devitrification in the glass. However, the presence of intermetallic products left by the reacted foil may degrade the mechanical properties of the joint. Because some of the characteristics of reactive foils (such as a negative heat of mixing of the components) are also characteristics of glass-forming alloys, it may be possible to design foils that react to form amorphous phases. To this end, we have investigated the heats of reaction, reaction velocities, and structure of Zr/Ni, Zr/Ni/Al, and Zr/(CuNi)/Al foils. We explore the influence of foil architecture on phase selection, and, in particular, on amorphous phase formation. We also discuss joining bulk metallic glasses using these reactive foils.

4:00 PM

Fabrication and Characterization of Ta-Based Amorphous Alloys: *Jiaping Wang*[1]; Laszlo J. Kecskes[2]; Todd C. Hufnagel[1]; [1]Johns Hopkins University, Matls. Sci. & Engrg., 102 Maryland Hall, 3400 N. Charles St., Baltimore, MD 21218 USA; [2]U. S. Army Research Laboratory, Aberdeen Proving Ground, MD 21005 USA

In most engineering applications low-density materials are desirable, but some specialized applications benefit from high-density materials. To this end, we have produced a series of Ta-Nb-(Fe,Ni) amorphous alloys with densities greater than 12 g cm-3 by mechanical alloying of the elemental powders. We have followed the progress of the amorphization by x-ray diffraction, scanning electron microscopy, and transmission electron microscopy. Thermal properties, including glass transition temperatures, crystallization temperatures, and liquidus temperatures were measured by differential scanning calorimetry and differential thermal analysis. We describe the mechanisms of amorphous alloy formation in the mechanically deformed powders, and the possibility of achieving even higher densities by making composite materials consisting of W particles in an amorphous Ta-alloy matrix.

4:20 PM

Consolidation of Fe-Based Amorphous Metal Powders by ECAE: Suveen N. Mathaudhu[1]; *K. Ted Hartwig*[1]; Ibrahim Karaman[1]; [1]Texas A&M University, Mechl. Engrg., 3123 TAMU, College Sta., TX 77843-3123 USA

Recent advances have allowed the fabrication of Fe-based bulk metallic glasses which have yield strengths two to three time that of common high strength steels. But limited structural applications have been found due to size limitations (~1 cm diameter max) inherent to the alloy systems used and the casting process. In this paper, hot equal channel angular extrusion (ECAE) in 90° tooling is used to consolidate Fe-based amorphous metal powder (Fe-Cr-Mo-Y-C-B) into a bulk amorphous metal rod with sizes equal to or greater than can be currently fabricated by casting. A fully dense and uniformly consolidated product is expected after only one extrusion. Hardness, DSC and other experimental results are reported.

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Nano-Hetero Structures in Zr-Base Glass Forming Alloys: *Jayanta Das*[1]; *Jürgen Eckert*[1]; Wolfgang Löser[2]; Sanat K. Roy[3]; Annett Gebert[2]; [1]Technische Universität Darmstadt, FB11 Matl. und Geowissenschaften, FG Physikalische Metallkunde, Petersenstrasse 23, Darmstadt D-64287 Germany; [2]Leibniz-Institut für Festkörper- und Werkstoffforschung Dresden, Postfach 270016, D-01171 Dresden Germany; [3]Indian Institute of Technology, Dept. of Metallurgl. & Matls. Engrg., Kharagpur 721302 India

Bulk metallic glasses and nanostructured Zr-base multicomponent alloys are attractive candidates for advanced high strength materials for structural applications as well as for possible use as functional materials. Typically the strength of such alloys can be significantly higher than the values achievable for conventional microcrystalline materials. However, one major drawback for the use in engineering applications is the often limited macroscopic plastic deformability at room temperature, despite the fact that some of these alloys show perfectly elastic-plastic deformation behavior. This feature is correlated with localized deformation process, where high plastic deformation processes is accumulated in a very narrow region without contributing to macroscopic plasticity. To avoid such limitations, the concept of heterogeneous microstructure with partly glassy or nanostructured matrix and different length scale of second-phase dispersions has been recently employed to toughen the bulk metallic glasses or nanostructured materials derived from glass forming alloy compositions. We will present recent results obtained from Zr-base multicomponent structural in situ composite materials with unusual microstructure synthesized in a bulk form through inexpensive processing routes. This type of composite microstructure is able to achieve high strength together with high ductility by controlling the instabilities responsible for early failure.

Carbon Technology: Green Anodes

Sponsored by: Light Metals Division, LMD-Aluminum Committee
Program Organizers: Todd W. Dixon, ConocoPhillips, Borger, TX 79007 USA; Halvor Kvande, Norsk Hydro ASA, Oslo N-0240 Norway; Markus Meier, R&D Carbon, Sierre CH 3960 Switzerland

Monday PM Room: 2007
February 14, 2005 Location: Moscone West Convention Center

Session Chairs: Matt Powell, Century Aluminum, Hawesville, KY 42348 USA; Zeno DeMori, Hilton Head Island, SC 29926 USA

2:00 PM
Capacity Creep Considerations for a Carbon Plant: *David William Glover*[1]; [1]Hatch Associates, 152 Wharf St., Brisbane Australia

Many smelters have been pursuing capacity creep to improve their economic position. As the amperage has been raised, the demand for raw materials such as power, alumina, and carbon has increased. Anode supply has become a constraint for many smelters and this paper is a discussion of the options, challenges, and opportunities available to smelters considering increasing their capacity.

2:25 PM
The Integration of Lean and Six Sigma - A Powerful Improvement Strategy for Carbon Plants: *Keith A. Sinclair*[1]; Rick Phelps[1]; Barry Sadler[2]; [1]Sinclair Associates, Inc., 12620 Ridgepath Ln., Knoxville, TN 37922 USA; [2]Net Carbon Consulting Pty Ltd., PO Box 286, Kangaroo Ground, Victoria 3097 Australia

Lean Manufacturing and Six Sigma have come to the forefront as models for manufacturing excellence. Six Sigma is driven from the strong relationship between reducing process/product variation and increasing business value - as represented by lead-time, cost, yield, and product quality. Lean Manufacturing is focused on the elimination of waste to reduce variation, shorten cycle times, accelerate product flow, and increase Customer "value in use." Although applied to some degree in Carbon Plants, they are not commonly used. The Authors feel there are several reasons for this: * Available information tends to focus on Lean/Six Sigma in discrete manufacturing. * There is little available experience in processes such as anode production. * Some concepts in Lean/Six Sigma have little relevance to existing Carbon Plants. These methods require careful integration to deliver full benefits - this is not always done well. Examples will be provided to demonstrate how Lean/Six Sigma can be successfully integrated into a wider framework and used to deliver sustained business value in process industries.

2:50 PM
Coke Quality Effect on the Grinding in the Air Swept Ball Mill Circuit: *Juraj Chmelar*[1]; Trygve Foosnæs[2]; Harald Arnljot Øye[2]; [1]SINTEF, Matls. & Chmst., Alfred Getz vei 2, Trondheim NO-7465 Norway; [2]NTNU, Dept. of Matls. Tech., Sem Sælands v 14, Trondheim NO-7491 Norway

Petroleum coke fines have been produced from three petrol coke qualities in an air swept ball mill with integrated air classifier under varying operating conditions. The pilot scale ball mill circuit is fully computer controlled with a laser based online particle size analyzer. The particle size is continuously monitored on a representative sample obtained from the air classifier outlet using a sample probe. The fines granulometry is specified through the computer controlling the ball mill circuit. The paper presents results obtained from the fines production with the following objectives; different product size, air sweeping velocity/particles residence time in the mill, circulating amount, mill throughput and specific energy consumption. The circulating load and air sweeping velocity/particle residence time has a critical effect on the particle size distribution steepness although the same top size product is produced. The morphology of the product was analyzed. The particle shape depends on the process control and the energy used for fines production.

3:15 PM
Fines Production for Anode Manufacturing: *Thore Moeller*[1]; [1]Claudius Peters Projects GmbH, Schanzenstrasse 40, 21614 Buxtehude Germany

For the anode production, 20-30% of the petroleum coke is used as dust in the fines fraction. Petroleum coke with an (HGI) 32-40 is ground to dust with 2000-5000 cm^2/g (Blaine) in a ball mill and are separated via the dynamic air swept classifier. During normal operation, these mills run during 60-90% of the time. When operating in shorter intervals the consistency of the dust fineness is not guaranteed. Operation with longer intervals and hence interruptions of several hours per shift, the segregation in the large silos of 30-50 ton capacity leads again to consistency problems. This presentation describes the operation of a vertical mill with integrated classifier for the anode industry, that was originally introduced in the coal and mineral industry. With this mill, dust can be produced during permanent operation which leads to consistent characteristics at minimum silo capacity.

3:40 PM Break

3:55 PM
Carbon Plant Performance with Blended Coke by Alberto Salvador: *Alberto Salvador Gomes*[1]; Reinhard Max Heilgendorff[1]; [1]ALBRAS Aluminio Brasileiro SA, Estrada Pa 483, Km 21, Vila Murucupi, Barcarena, Para 68447-000 Brazil

Quality deterioration and variability in the calcined coke market have resulted in routine changes in the property set of coke supplied to Albras. This deterioration has encouraged Albras to in investigate on-site, calcined coke blending and the consequent impact on carbon plant operation. This paper presents the results of industrial-scale testing of an on-site blend of two cokes - each produced from a single green coke.

4:20 PM
Finer Fines in Anode Formulation: *Francisco Figueiredo*[1]; [1]Consórcio de Alumínio do Maranhão, Smelter, BR 135, km 18, Electrode Dept., São Luís, MA 65095-604 Brazil

In order to provide continuous improvement and permit amperage increase in Potrooms, many efforts have been conducted to optimize anode formulation at Alumar. At the same time this new technique is an alternative to compensate calcined coke VBD (vibrated bulk density) deterioration. Carbon plant department studied the effect of finer fines in anode formulation and conducted trials to confirm observations. Green mill operation and process parameters were adjusted to increase 400 points in Blaine measurement (R&D Carbon Method). Results were measured in terms of green and baked anode properties. Baked apparent density, air permeability, electrical resistivity and flexural strength improved as expected with high statistical correlation. No cracks rate increase was observed and baked loss was the lowest in plant history.

4:45 PM
The SCAP-Rhodax® Process for Dry Mix Preparation in Anodes Plants: *Andre Pinoncely*[1]; Corinne Jouault[2]; Jean-Francois Andre[1]; Yann El Ghaoui[2]; Jean-Christophe Rotger[2]; Christian Dreyer[3]; [1]Solios Carbone, 32 rue Fleury Neuvesel, Givors 69702 France; [2]Alcan, LRF, St. Jean De Maurienne 73303 France; [3]Aluminium Dunkerque, Zip Ouest, Loon Plage 59279 France

Anode manufacturers have to ensure that their anode quality will allow a safe and optimum potline operation. This high anode quality must be obtained at the lowest price. The Solios Carbone Aluminium Pechiney - Rhodax® process, or SCAP-Rhodax®, which is dedicated to the production of a dry mix with an optimized G/S ratio, was developed following two objectives: reduce the investment and operating costs and ensure a high and stable anode quality. The final step of the Alcan and Solios Carbone research program was the construction of an industrial scale 35 tph pilot plant, which namely incorporates the use of a Rhodax® crusher, at the Aluminium Dunkerque smelter in France. This pilot plant allowed, from 2002 to 2004, the full validation of this very innovative process. Since May 2004, the SCAP-Rhodax® process ensures the whole anode production of the Aluminium Dunkerque smelter, on a continuous way. This process lead to a real breakthrough in paste plant technology and Aluminium Bahrain has already chosen it for its line 5 expansion. This new 35 tph industrial SCAP-Rhodax® reference will start up at the end of 2004. This paper recalls the process flow sheet, gives an updated synthesis of the industrial results demonstrated at the Aluminium Dunkerque prototype, and draws up the main figures of the first commercial reference coming soon on stream at Alba line 5.

Cast Shop Technology: Aluminum Melting: Strategies and Sourcing

Sponsored by: Light Metals Division, LMD-Aluminum Committee
Program Organizers: Gerd Ulrich Gruen, Hydro Aluminium AS, Bonn 53117 Germany; Corleen Chesonis, Alcoa Inc., Alcoa Technical Center, Alcoa Center, PA 15069 USA; Halvor Kvande, Norsk Hydro ASA, Oslo N-0240 Norway

Monday PM Room: 2001
February 14, 2005 Location: Moscone West Convention Center

Session Chairs: Subodh K. Das, Secat Inc., Ctr. for Al Tech., Lexington, KY 40511 USA; Paul King, Albany Research Center, Albany, OR 97321 USA

2:00 PM
Implications of the Changing World of Aluminum Metal Supply: *Subodh K. Das*[1]; W. Jerry Long[1]; H. Wayne Hayden[2]; John A.S. Green[4]; [1]Secat , Inc., 1505 Bull Lea Rd., Lexington, KY 40511 USA; [2]MMPaCT, 123 Lake Hill Dr., Oak Ridge, TN 37830-4231 USA; [4]Consultant, 3712 Tustin Rd., Ellicott City, MD 21042-4826 USA

Geographic distribution of aluminum production has shifted, driven by energy and raw materials factors, and this transformation will likely continue in the future. A scenario for the U.S. aluminum industry is presented that illustrates the increasing impact of remelting, as compared to primary production by smelting of aluminum in the next few decades, with an emphasis on the magnitude of the opportunity for energy savings in each area. In the U.S., consumption will continue to grow while primary production will continue to shrink. Thus, the supply of metal to downstream fabrication processes will need to be increasingly met from re-melted ingot and scrap sources. Energy-efficient technologies for remelting and fabrication will play a more pivotal role in reducing energy consumption, environmental impacts, and imports. Areas of suggested research topics in the broad field of recycling, remelting and fabrication will be discussed as they apply to the changing aluminum world. Adapted from work originally appearing in August 2004 issue of *JOM*, pages 14-17.

2:25 PM
Scheduling Optimisation for Aluminium Smelter: *Neil Freeman*[1]; Jeffrey Dean Kelly[2]; [1]Honeywell, HPS, 5 Kitchener Way, Perth, Western Australia 6101 Australia; [2]Honeywell, Process Solutions, 300 Yorkland Blvd., N. York, Ontario M2J 1S1 Canada

Scheduling of cast house operations is difficult especially for multi-product casting operations. The cast house operations are generally batch oriented where as the pot line operations continuously produce hot metal which must be processed. This results in difficulties coordinating the pot line operations with the cast house operations with the net effect being sub optimal scheduling. New technologies incorporating Mixed Integer Linear Programming are able to not only solve this "closed" shop scheduling problem but also optimise this from both a logistics and quality perspective to minimise costs and maximise profit. There are considerable gains to be realised by optimally scheduling the flow of hot metal from reduction lines through the casthouse, particularly for multi-product casting operations. These gains will come from work flow improvements as well as melt loss minimisation, pot line superheat re-use, product quality enhancements and stock holding reductions. This paper discusses the problem, solution technology and benefits to be gained from scheduling optimisation. Additionally a case study will be presented where the technology has been successfully applied.

2:50 PM
Detection of Water Content in Aluminum Scraps with a Fast Neutron Source (Cf-252): *Miting Du*[2]; Qingyou Han[1]; Ray D. Peterson[3]; [1]Oak Ridge National Laboratory, Metals & Ceram. Div., One Bethel Valley, Oak Ridge, TN 37831-6083 USA; [2]Oak Ridge National Laboratory, Nucl. Sci. & Tech. Div., One Bethel Valley, Oak Ridge, TN 37831-6385 USA; [3]IMCO Recycling, Inc, 397 Black Hollow Rd., Rockwood, TN 37854 USA

Aluminum scrap and remelt secondary ingot (RSI) may contain water in their internal voids. The presence of water can be a serious safety issue for the aluminum remelting industries. This article describes a method that utilizes neutrons for the rapid detection of water in solid aluminum materials based on the fact that neutrons interact with hydrogen atoms in the water molecules. A fast neutron source (252Cf) and a portable "slow-down" (backscattering) neutron detector are used for moisture detection. Initial experiments carried out with aluminum turnings indicate that there is a linear relationship between the detected slow neutron counts and the hydrogen/water levels in aluminum scrap. The method has the potential of being used by the aluminum remelting industries for rapid, non-destructive detection of water in aluminum scrap or RSI.

3:15 PM
Quantifying Economic and Scrap Usage Impacts of Operational Uncertainty Within Alloy Production Planning: *Preston P. Li*[1]; Randolph E. Kirchain[1]; [1]Massachusetts Institute of Technology, Matls. Sys. Lab., Rm. E40-421, 77 Mass. Ave., Cambridge, MA 02139 USA

The intensive recovery and recycling of scrap will certainly play a central role in the long-term sustainable use of light metals. Yet, recognizing that producers are economic agents, environmental arguments alone are insufficient to promote scrap purchase and usage. Such efforts must be paralleled by economic incentives. This paper examines the potential for more efficient raw materials management through explicit consideration of operational uncertainties (e.g., uncertain demand for products) during production planning. Such uncertainties are considered within a two-stage recourse optimization framework. Both a conceptual framework and hypothetical case studies are presented, which demonstrate overall financial benefits and specific economic incentives for greater scrap use for aluminum alloy production. Case results also demonstrate that, although intuitive, alloy production planning based solely on expected outcomes leads to more costly production than planning derived from more robust analytical methods. By factoring in the penalties associated with different possible outcomes, the new scrap purchasing decisions better positioned the alloy producer to weather uncertain outcomes and promoted greater scrap reuse efficiency.

3:40 PM Break

3:50 PM
Industrial Application of Furnace Heel and Transferred Weight Measurement: *John Courtenay*[1]; Cees Castelijns[2]; Marcel Vossenberg[2]; [1]MQP Limited, 6, Hallcroft Way, Knowle, Solihull, W. Midlands B93 9EW UK; [2]Corus Aluminium NV, A. Stoccietlaan 87, 2570, Duffel Belgium

A new system for measuring the heel and transferred weight with an accuracy of +/-200kg has been developed and applied industrially at the Duffel works of Corus Aluminium N V in Belgium on a 50 tonne tilting holding furnace. The system, known as BatchPilot, was developed by BDH Tech of Chicoutimi and works on the principle of measuring changes in the hydraulic pressure in the furnace main cylinder. Since December 2003 a unit has been on industrial trial at Duffel and during June 2004 performance reached design values. The equipment has since been placed into full production usage with excellent results with respect to accuracy being achieved. The objective at Corus is to improve yield through reduction in the number of over length casts. The paper describes the technology and developments made during the trial period to improve operator friendliness and accuracy. The collection of data, its interpretation and inter-relation with furnace batching procedure are reviewed.

4:15 PM
EMIX+ Revolutionizes Circulation and Transfer of Liquid Aluminium in Furnaces: *Owen Stephen Tollerfield*[1]; [1]Solios Thermal, Ops., Midland House, Ounsdale Rd., Wombourne, Wolverhampton, W. Midlands WV5 8BY England

Solios Thermal have completed the successful production start-up of their EMIX+ system, to displace liquid aluminium in a 20-Tonne capacity Sidewell Furnace. The vertical component of the EMIX+ not only facilitates full bath circulation and clean scrap submergence, but also controlled transfer. As such, it has the potential to eliminate the tilting furnace altogether. First indications have also shown high circulation rates and rapid submergence of light-weight, de-coated scrap and silicon alloy chips. Results include increased metal recovery rates, increased alloy dissolution rates and decreased batch times. This paper confirms the effectiveness of the EMIX+ in the cast house environment. Field results are presented to reinforce and confirm all theoretical aspects. With intrinsic safety, low maintenance requirements (no moving parts) and total flexibility, the EMIX+ presents a revolutionary solution to electromagnetic stirring and transferring. Solios Thermal will continue to develop the EMIX+ for both the primary and secondary aluminium sectors.

Cast Shop Technology: Melt Treatment: Fluxing, Alloying and Grain Refinement

Sponsored by: Light Metals Division, LMD-Aluminum Committee
Program Organizers: Gerd Ulrich Gruen, Hydro Aluminium AS, Bonn 53117 Germany; Corleen Chesonis, Alcoa Inc., Alcoa Technical Center, Alcoa Center, PA 15069 USA; Halvor Kvande, Norsk Hydro ASA, Oslo N-0240 Norway

Monday PM Room: 2002
February 14, 2005 Location: Moscone West Convention Center

Session Chair: Christian Pluchon, Alcan Pechiney CRV, Unité de Recherche Fonderie, Voreppe 38340 France

2:00 PM
Mathematical Modeling of the Chlorine Fluxing of Aluminum: *Autumn Fjeld*[1]; Suchitra Edussuriya[1]; James W. Evans[1]; Aniruddha Mukhopadhyay[2]; [1]University of California, Matls. Sci. & Engrg., 210 Hearst Mining Bldg., MS 1760, Berkely, CA 94720 USA; [2]FLUENT

Chlorine fluxing is an essential process in the removal of impurities from aluminum, e.g. Na, Li in the primary aluminum industry and Mg in the secondary industry. Such impurities are removed by injecting a mixture of chlorine and argon gas below the surface of the molten aluminum. In some cases this is done using simple tubes ("wands" or "lances"), but more sophisticated devices have been developed where the gas is injected through a rotating impeller which simultaneously agitates the melt, while breaking up and dispersing gas bubbles throughout the liquid. Ideally, the chlorine in the bubbles reacts with the impurities to form solid or liquid chloride layers floating on the aluminum. In reality, however, much of the injected chlorine reacts to form gaseous aluminum chloride. In turn, some of this byproduct reacts with the impurities in the melt. This reaction scheme introduces inefficiency into the process as a fraction of the aluminum chloride escapes without reacting. Thus, product is lost and the aluminum chloride reacts with atmospheric moisture to produce HCl emissions. This inefficiency is dependent upon factors such as the residence time of bubbles in the melt and the surface area of the bubbles. In previous issues of Light Metals we have described a capacitance probe used to measure bubbles in liquid aluminum and its use in an A622 fluxing unit at Alcoa. In the present paper we describe a mathematical model designed to complement the experimental measurements. At the heart of the model is the computation of liquid and gas velocities using the software FLUENT®. This computational fluid dynamics package computes the velocities in the realistic 3D geometry for the turbulent two-phase flow. Bubble residence time distributions and gas fraction at various points in the melt are also computed. The former are important in that they are then coupled to a model for the reaction to predict chlorine utilization efficiency; the latter are valuable because they allow comparison with the capacitance probe measurements. Research supported by DOE under grant DE-FC07-01ID14192.

2:25 PM
The Choice of Additions to NaCl-KCl Mixture for Aluminum Refining from Alkali and Alkali-Earth Impurities: Anatoly Georgievich Zholnin[1]; *Sergey Borisovich Novichkov*[2]; Alexander Georgievich Stroganov[1]; [1]Mosoblprommontazh, der.Ratmirovo, Ul.Naberezhnaya, 4, Voskresensky region, Moscovskay oblast 140207 Russia; [2]Russkiy Aluminiy, Prokatniy Div., Verhniy Taganskiy Typic, 4, Moscow Russia

By thermodynamic calculation was shown that the fluoride additions of alkali and alkali-earth elements to the NaCl-KCl equiweight mixture lead to the formation of any quantity of NaF in the flux. The formation of NaF leads to the aluminum saturation with sodium. The more equilibrium concentration of NaF in the flux, the more is equilibrium concentration of sodium in aluminum. Therefore all fluoride additions of alkali and alkali-earth elements lead to the aluminum saturation with sodium. The design data was confirmed experimentally on the crucible fusions. In contrast to the fluoride of alkali and alkali-earth elements, the AlF3 addition dos not result to the formation of NaF in the flux. The AlF3 addition efficiently reduces the content of sodium in aluminum, but it is very expensive. At the same time, it was experimentally discovered, that the negative influence of fluoride additions of alkali and alkali-earth elements on the sodium saturation may be neutralized by MgCl2.

2:50 PM
Evaluation of Molten Metal Losses Using Flux Protecting Covers: *Alfredo Flores Valdés*[1]; *José Escobedo Bocardo*[1]; Fidel Barajas Guevara[1]; [1]CINVESTAV, Metall., Manzana 18, #100, Fraccionamiento Molinos del Rey, Ramos Arizpe, Coahuila 25900 México

This work describes a statistically designed experimental procedure for the development of molten aluminum protecting fluxes. The composition of fluxes was based on the equimolar NaCl-KCl composition, adding to complete the formulation different amounts of fluorides such as NaF, KF, LiF, and Na3AlF6. Regarding the results obtained at a laboratory scale, the best performance was registered for a formulation containing 90 wt % NaCl-KCl, plus 10 wt % Na3AlF6, as the molten metal losses reduced from around 12 wt % to around 5 wt %. Furthermore, this formulation was tested at industrial trials level in a 4000 kg molten aluminum capacity reverberatory furnace, reducing the molten metal losses from around 10 wt % to less than 6 wt %.

3:15 PM
A Methodology for Analyzing Se in Mn Electrolytic Metal and Al Materials Coming From the Casthouse: Raquel Antolín[1]; Tomás Posada[1]; *Gregorio Borge*[1]; Juan Carlos Raposo[1]; Gorka Arana[2]; Nestor Etxebarria[2]; [1]Bostlan, S.A., Techl. Dept., Poligo Industrial Trobika, s/n, Mungia 48100 Spain; [2]University of the Basque Country, Analytical Chmst., POB 644, Bilbao 48080 Spain

Production of Mn electrolytic metal can be improved by the addition of selenium derivatives. Se is then added to the production of aluminium when Mn compacts are added to the molten bath in the casthouse. Problems related to Se toxicity during aluminium processing, and specially during the recycling of aluminium drosses, have been reported in the last years at different TMS conferences. In spite of this, actual content of Se is rarely certified or even reported in the documentation supplied by Mn electrolytic metal producers, although Se concentrations are essential to classify Mn lots. This work tries to solve controversies about real content of Se in Mn additives with the development of an analytical method HG-ICP-OES (hydride generation-inductively coupled plasma-optical emission spectroscopy) which is inexpensive, easy to handle and adequate in terms of high sensibility and reproducibility for industrial metallic matrixes. A laboratory reference material (LRM) of Se in electrolytic Mn has been generated to verify the goodness of the measurements performed. The new methodology allows to control precisely and accurately the Se concentration in Mn raw material lots, and in Al baths and drosses, thus a more adequate answer to issues of Se fate in aluminium production chain can be given.

Characterization of Minerals, Metals and Materials: Characterization of Structural Engineering Materials - I

Sponsored by: Extraction & Processing Division, EPD-Materials Characterization Committee
Program Organizers: Tzong T. Chen, Natural Resources Canada, CANMET, Ottawa, Ontario K1A 0G1 Canada; Ann M. Hagni, Construction Technology Laboratories, Inc., Microscopy Group, Skokie, IL 60077 USA; J. Y. Hwang, Michigan Technological University, Institute of Materials Processing, Houghton, MI 49931-1295 USA

Monday PM Room: 2010
February 14, 2005 Location: Moscone West Convention Center

Session Chairs: Masafumi Maeda, University of Tokyo, Inst. of Industl. Sci., Tokyo 153-8505 Japan; Donato Firrao, Politecnico di Torino, Dip. di Scienza dei Materiali e Ingegneria Chimica, Torino 10129 Italy

2:00 PM
The Effect of Delta-Ferrite in P92 Steel on the Formation of Laves Phase and Cavities for the Reduction of Fatigue Life: *Jung Woong Baek*[1]; Soo Woo Nam[1]; [1]Korea Advanced Institute of Science and Technology, Matls. Sci. & Engrg., 373-1, Guseong-dong, Yuseong-gu, Daejeon 305-701 S. Korea

Modern tempered martensite 9~12%Cr steels are introduced as excellent materials for power generation. Although the 9~12%Cr steels have fully martensite microstructure, they have some tendency to form the delta-ferrite during welding and other procedure. It is known that delta-ferrite has harmful effects on the high temperature mechanical properties because of its poor creep ductility and toughness. Compared with inside of grain, grain boundaries are the preferential sites for precipitation of second phase particles, however it is confirmed from analyses of microstructural observation and diffraction

pattern that Laves phase is preferentially formed inside of delta-ferrite rather than lath boundary and inside of martensite. Therefore, creep cavities are found to be formed along the Laves phase interface during creep-fatigue test. It is hypothesized that the brittle Laves phase is responsible for the reduction of the creep-fatigue life by the formation of creep damage of cavities.

2:25 PM
Analyses of Stress Corrosion Cracking in X-52 Steel Line-Pipes: *Jian Li*[1]; Mimoun Elboujdaini[1]; [1]Natural Resources Canada, CANMET-MTL, 568 Booth St., Ottawa, Ontario K1A 0G1 Canada

Failures of X-52 steel line-pipes due to stress corrosion cracking (SCC) have been a primary concern in oil and gas industry. However, the mechanisms of crack initiation and propagation have not been well understood. In this work, SCC from a section of line-pipe was thoroughly investigated. Features of intergranular cracks (IGSCC) and transgranular cracks (TGSCC) were characterized with optical microcopy, scanning electron microscopy (SEM), focused ion beam (FIB) microscopy and transmission electron microscopy (TEM). The effect of carbide on crack propagation is emphasized.

2:50 PM
Effect of Heat Treatment on the Microstructure and Texture Evolution of Modfied 316LN Stainless Steel: *Steven T. Downey*[1]; Peter N. Kalu[1]; Ke Han[2]; [1]FAMU/FSU College of Engineering, Dept. of Mechl. Engrg., 2525 Pottsdamer St., Tallahassee, FL 32310-6046 Leon ; [2]National High Magnetic Field Laboratory, Magnet Sci. & Tech., 1800 E. Paul Dirac Dr., Tallahassee, FL 32301 USA

Chemically modified 316LN Stainless steel is currently used by the National High Magnetic Field Laboratory to jacket superconductors used in the Superconducting Outsert Conduit of the 45T Hybrid Magnet System. The principal reason for using this material is its ability to withstand the effects of the Nb3Sn reaction heat treatment. This investigation focuses on the effect of heat treatment on the microstructure and texture evolution of the modified 316LN stainless steel. Optical microscopy, X-Ray texture, ESEM and related electron microscopical tools were employed for the analysis. Although annealing at 700°C, for times ranging from 1 to 100 hours, resulted in a negligible grain growth and texture change, there was substantial increase in precipitate formation. A correlation between the heat treatment and the microstructural and texture development is presented.

3:15 PM
Effect of Cryogenic Treatment on the Mechanical Properties of Steel (4340) and Aluminum Alloy (7075): *Saeed Zhirafar*[1]; Martin Pugh[1]; [1]Concordia University, Dept. of Mechl. & Industrial Engrg., 1455 de Maisonneuve Blvd. W., Montreal, Quebec H3G 1M8 Canada

Over the last few years, interest has been shown in the effect of very low temperatures during the heat treatment cycle on the performance of the steels. “Cryogenic Tempering” the process of deep-freezing materials at Cryogenic temperatures (-196°C), has been reported to optimize the mechanical properties of some steels, normally tool steels, being treated. This paper reports on experiments carried out to determine the hardness, toughness and durability of cryogenically treated Steel (4340) and Aluminum alloy (7075) as compared to those conventionally treated.

3:40 PM Break

3:50 PM
Imaging of Deformation Microstructure in Ni-Based Superalloys: *Peter Maxwell Sarosi*[1]; Gopal Babu Viswanathan[1]; Deborah Whitis[2]; Michael Mills[1]; Raymond Unocic[1]; [1]Ohio State University, Matls. Sci. & Engrg., 477 Watts Hall, 2041 College Rd., Columbus, OH 43210 USA; [2]AEGE, Matls. Sci. & Engrg., Cincinnati, OH USA

The exellent creep tensile, fatigue and crack growth properties of nickel based superalloys have made them the favored, high temperature structural material used in the turbine section of jet engines. However, higher operating temperatures needed to increase enige efficiency degrade the superalloy’s structural properties including creep. The creep deformation mechanisms in these alloys can be complex with different deformations mechanisms arising as a function of applied stress temperature and microstructure. Computer simulations of HRTEM images and bright field images of stacking faults were compared with experimental results in order to determine the nature of the stacking faults which are necessary for the development of physically based creep models.

4:15 PM
Vapor Pressure Measurement of Phosphorous in Molten Carbon Saturated Iron: *Takashi Nagai*[1]; Masao Miyake[1]; Hisao Kimura[1]; Masafumi Maeda[1]; [1]University of Tokyo, Inst. of Industrial Sci., Internatl. Rsch. Ctr. for Sustainable Matls., 4-6-1 Komaba, Meguro, Tokyo 153-8505 Japan

The hot metal pretreatment is common practice for dephosphorization. To develop more effective process, reliable thermodynamic data of phosphorous in molten carbon saturated iron is required. In this research, thermodynamic properties of phosphorous in molten iron were investigated. The vapor pressure of P2 in equilibrium with carbon-saturated molten iron containing phosphorous was measured by double Knudsen cell mass spectrometry. The measurements revealed that the activity of phosphorous in molten iron saturated with carbon obeys Henry’s law in the range of phosphorous content below 0.72 wt%.

4:40 PM
An EBSD Study of Oxidation Behavior of Iron-Base Alloy in Supercritical Water Reactor: *Lizhen Tan*[1]; Todd R. Allen[1]; [1]University of Wisconsin, Dept. of Engrg. Physics, 1500 Engrg. Dr., Madison, WI 53706 USA

The supercritical-water-cooled reactor (SCWR) system is recommended in the DOE Generation IV reactor program due to its high thermal efficiency and plant simplification. At supercritical water conditions of 500°C and 25 MPa, one of the properties of most concern for materials selection is oxidation behavior. This behavior is generally evaluated by means of weight or thickness change. In this work, a new analytical method, electron backscatter diffraction, was employed to study the oxidation behavior of alloys exposed to SCW. Microstructural evolution including phase, grain size and shape, and texture, from bulk to the interface between oxides and SCW is revealed by this technique. This methodology is important to understand oxidation mechanisms and sheds light on the study of the effect of Grain Boundary Engineering on oxidation resistance.

5:05 PM
Precipitates Characterization of Forged and Direct Quenched Ti-Nb-V HSLA Steels: *Y. Sikaddour*[1]; M. Hadji[2]; [1]Université des Sciences et de la Technologie Houari Boumedienne (USHB), Faculté de Génie Mécanique & Génie des Procédés, Dépt. des Scis. des Matériaux, BP 32 EL Alia Bab, Ezzouar 16000 Alger; [2]Université de Blida, Dépt. des Scis. des Matériaux, El Soumaa Blida 09000

The mechanical properties of HSLA steels depend mainly on the state and the forms of precipitates induced by their thermoméchanical history. The investigation reported here is a characterisation of precipitates in forged and direct quenched Ti-Nb-V HSLA steels. The objective is to develop microalloys forging steels in order to enhance mechanical properties of the hot formed steels parts while simultaneously eliminate the need for heat treatment of the steel, which can reduces energy consumption and processing time as well as the material inventories resulting from intermediate processing steps. It has been shown that the precipitates formed between 900° and 1100°C are essentially the fine TiN and Ti Carbonitrides (Ti (C,N)) which are more stable at high temperature than other microalloying carbides or nitrides and can therefore control the austenite grain size.The experiments revealed, however, the presence of sulfide (Mn,Ti) S and carbosulfide $Ti4C_2S_2$ which doesn’t contribute to the precipitation hardening in 0,25% Ti alloy and not in other % Ti alloys this, explain the hardness decrease. Many kinds of precipitates in spherical and lengthen forms are observed in grain boundary, it was essentially (Ti,C) N , Nb (C,N) and very complexes Carbonitrides; which retain austenite grain growth during thermomechanical treatment at high temperature. Titanium additions and the effect of the temperature forging are also investigated.

Characterization of Minerals, Metals and Materials: Characterization of Industrial Products

Sponsored by: Extraction & Processing Division, EPD-Materials Characterization Committee
Program Organizers: Tzong T. Chen, Natural Resources Canada, CANMET, Ottawa, Ontario K1A 0G1 Canada; Ann M. Hagni, Construction Technology Laboratories, Inc., Microscopy Group, Skokie, IL 60077 USA; J. Y. Hwang, Michigan Technological University, Institute of Materials Processing, Houghton, MI 49931-1295 USA

Monday PM Room: 2012
February 14, 2005 Location: Moscone West Convention Center

Session Chairs: Louis J. Cabri, Cabri Consulting Inc., Ottawa, Ontario K1S 5P5 Canada; Markus A. Reuter, Delft University of Technology, Delft 2628 RX Netherlands

2:00 PM
Characterization of Waelz Kiln Products from the Recycling of EAF Dust: *Tzong T. Chen*[1]; John E. Dutrizac[1]; Glenn Poirier[1]; [1]Natural Resources Canada, CANMET-MMSL, 555 Booth St., Ottawa, Ontario K1A 0G1 Canada

The Waelz kiln process is currently the most efficient commercial technique for processing EAF dust to recover the contained zinc as zinc oxide. In this process, EAF dust is converted to a Fe-rich slag and a Zn-rich Waelz oxide that is subsequently processed for the recovery of zinc. Grab samples from an European zinc recycling plant were studied. The EAF dust contains ~27% Zn which occurs mainly as ZnO and ZnFe2O4. During processing, the Zn is converted to ZnO, together with minor amounts of Pb(OH)Cl, PbCl2, NaCl and KCl, in the Waelz oxide product. The Fe is converted to metallic Fe, Fe oxide and FeO(OH), together with gypsum, CaO/Ca(OH)2, Ca2SiO4, Mn-Fe oxide, various other oxides and Ca-Al-Fe-Mg-Mn silicates, in the slag.

2:25 PM
Characterization of In-Service Concrete and Construction Materials for Failure Analyses and Performance Evaluation: *Ann Marisa Hagni*[1]; [1]Construction Technology Laboratories, Inc., Microscopy Grp., 5400 Old Orchard Rd., Skokie, IL 60077 USA

Construction materials that have been placed into service are routinely analyzed to determine cause of failure, distress, deterioration, or change in physical appearance. This information is used to evaluate the existing condition, as well as the expected future performance, of the concrete or other construction material. Optical microscopy, SEM-EDS, and XRD are key tools in identifying freeze-thaw damage, corrosion of steel reinforcement, chemical attack (sulfate, acid, alkaline), alkali-aggregate reaction, and shrinkage/swelling (plastic shrinkage, thermal expansion) in concrete. Raw materials, such as aggregates, are analyzed by mineralogical techniques to determine deleterious constituents. Cement and clinker feed materials are evaluated to optimize processing and final product, and water/cement ratio and air-void contents in concrete are determined by petrography during product development and after years of service. Examples of identification and significance of construction materials, and how mineralogical techniques are uniquely utilized in problem solving, will be discussed.

2:50 PM
Characterization of Pigments Produced by Soft-Chemical Methods: Azucena Arellano[1]; Sandra Bribiesca[1]; *Moisés A. Carreón*[1]; [1]Universidad Michoacana de San Nicolás de Hidalgo, Inst. de Investigaciones Metalúrgicas, Edificio, CP 58000, Morelia, Michoacán México

In the present work both physical and chemical characterization of black pigments synthesized via co-precipitation of Fe, Mn and Co nitrates is made. The effect of synthesis pH and the effect of chemical synthesis environment was studied. The resultant phases were characterized by means of XRD, IR spectroscopy, SEM, EDS and nitrogen porosimetry. It was found that the electrokinetic behavior of the metallic species in solution as well as the chemical environment (i.e. oxidant or inert) played a critical role in the final textural, compositional and morphological properties of the resultant pigments. XRD showed the formation of hematite when the synthesis was conducted on inert environment and magnetite in oxidant environment. SEM studies allowed us to study the effect of pH on the morphology of the synthesized phases.

3:15 PM
Fracture Mode Analysis of Phosphor Bronze Dropper Clamp in Railway Catenary System: Jung-Nam Kim[1]; *Jeongguk Kim*[1]; Song-Chul Lim[2]; Kae-Myung Kang[2]; Sung-Tae Kwon[1]; [1]Korea Railroad Research Institute, Railroad Safety Rsch. & Testing Ctr., 360-1 Woulam, Uiwang, Kyunggi 437-757 S. Korea; [2]Seoul National University of Technology, Matls. Sci. & Engrg., Seoul 139-743 S. Korea

Failure mode analysis was performed for phosphor bronze dropper clamp (DC), which is used as a holder between messenger wire and contact wire in railway catenary system. Several analysis techniques were employed for two different types of samples, a fractured DC during service and as-received new DC, to investigate the fracture mode of the DC. The chemical composition analysis of the DC was conducted to evaluate the chemical quality of the DC, and mechanical tests such as tension withstand strength test and holding strength test, were performed to verify the standard values. After mechanical testing, Scanning electron microscopy (SEM) characterizations with the energy dispersive X-ray (EDX) analyses were performed to observe the fracture surfaces of two samples. Through the SEM characterization of fracture surfaces, it was observed that the in-service fractured DC sample experienced stress corrosion cracking due to corrosive environment during service, while the tension tested sample showed ductile fracture morphology with dimples.

3:40 PM Break

3:50 PM
Characterization of Mold Fluxes for Continuous Casting of Steel: *Danny Rao Pratap Singh*[1]; E. Wei[1]; Y. D. Yang[1]; C. Feng[1]; I. D. Sommerville[1]; A. McLean[1]; [1]University of Toronto, Matls. Sci. & Engrg., 184 College St., Toronto, Ontario M5S 3E4 Canada

During continuous casting of steel, the properties of mold fluxes strongly affect the casting performance, steel quality and environment of the casting operation. In this study, a high temperature microscopy technique was used to investigate the melting behavior of mold fluxes, and a drip test method was used to determine their melting rate. The results showed that free carbon was a dominant factor in governing the melting behavior of the fluxes, and the melting rate increased with increasing carbon reactivity and with decreasing carbon content.

4:15 PM
Research Methods of Iron Ore Sinters: Improvement in their Quality Assessment: *Marilia Sacramento de Magalhaes*[1]; Roberto Parreiras Tavares[2]; Paulo Roberto Gomes Brandao[1]; [1]Federal University of Minas Gerais - UFMG, Mining Engrg. Dept., Rua Espírito Santo, 35/721, Belo Horizonte, MG 30160-030 Brazil; [2]Federal University of Minas Gerais - UFMG, Metallurgl. & Matls. Engrg. Dept., Rua Espírito Santo, 35, Belo Horizonte, MG 30160-030 Brazil

Iron ore sinters are the main burden of blast furnaces for pig iron production. The evaluation of these agglomerates is very important due to their properties affect indirectly the productivity and costs of production of the steel industry. Besides classical methods commonly used in sintering plants: particle size evaluation, bulk chemical analyses, tumbler and/or shatter tests and reduction degradation and reducibility indexes, microscopy techniques allow to enhance the sintering process assessment. For investigation of the phases and microstructures, reflected-light and backscattered electrons images were used; for microanalytical chemical examination, energy-dispersive X-ray spectrometry; for Kikuchi patterns registers, electron backscattering diffraction. As complementary data, magnetic susceptibility measurements were applied to characterize the magnetic behavior. Hematite, magnetite, silicoferrite of calcium and aluminium and silicates are formed during the sintering. Hematite and Mg-bearing silicate are also remnants of ores and fluxes, respectively. Phase associations and their proportions are some aspects appraised by such procedures.

4:40 PM
Quantitative Characterization of Phases Present in Aluminum Drosses: *Adriana Gómez Gómez*[1]; Nelson Batista de Lima[2]; Jorge Alberto Soares Tenório[1]; [1]Escola Politécnica - Universidade de São Paulo, Metallurgl. & Matls. Engrg., Av. Prof. Mello Moraes, 2463, São Paulo, São Paulo 05508-900 Brasil; [2]Instituto de Pesquisas Energéticas e Nucleares, X-Ray Diffraction Lab., Av. Lineu Prestes, 2242, São Paulo, São Paulo Brasil

The white dross is a result of the aluminum oxidation during its primary production. White dross is mainly composed of metallic aluminum, Al2O3, with minor amounts of AlN and some oxides. This great variety of phases does complicated the quantitative characterization. This work shows a quantitative method to determine the main phases of white aluminum drosses by means of X-ray diffraction (the Rietveld Method). Actually, the Rietveld Method is maybe the most

useful method for obtaining quantitative phases information in multi-component mixtures, this method permits relatively quick quantitative phase analysis by fitting the calculated X-ray diffraction profile with the observed one. The analyses were done for the material smaller than 45 micron, to obtain the suitable material size the aluminum dross was grounded by ten minutes, several times. The grounded material was screened, and the material smaller than 45 micron was taken to quantitative XRD analysis.

5:05 PM
Rheological Characterization of Viscoelastic Composite Systems Used in Oil Industry: *Sayavur Ispandiyar Bakhtiyarov*[1]; Geilani M. Panahov[2]; Eldar M. Abbasov[2]; [1]Auburn University, Mechl. Engrg., 202 Ross Hall, Auburn, AL 36849-5341 USA; [2]Azerbaijan National Academy of Sciences, Inst. of Math. & Math., Baku Azerbaijan

Currently the oil industry requires a development and application more "smart" materials, which will resist high range of temperatures and pressures, shear conditions, and chemical environment. Application of "self-healing" viscoelastic composite materials in many technological processes of oil production has been proven to increase an efficiency and quality of the operations. Unfortunately, the rheological and transport properties of these composite materials were not studied sufficiently. In this paper we present the results of the development of optimal recipes of thixotropic viscoelastic composite material with "self-recoverable" properties. A systematic and fundamental study of rheophysical properties and hydrodynamic behavior of composite material is realized in these studies. Laboratory experiments were carried out to determine important thermophysical, rheological and mechanical properties of the test materials using both the standard commercial and in-house made equipment. The obtained results provide a valuable information for computer modeling of the viscoelastic fluid flow in pipes of complex geometry.

Computational Aspects of Mechanical Properties of Materials: Atomistic-Scale Modeling

Sponsored by: Materials Processing and Manufacturing Division, MPMD-Computational Materials Science & Engineering-(Jt. ASM-MSCTS)
Program Organizers: Kwai S. Chan, Southwest Research Institute, Department of Materials Science, San Antonio, TX 78284 USA; Diana Farkas, Virginia Polytechnic Institute and State University, Department of Materials Science and Engineering, Blacksburg, VA 24061 USA

Monday PM Room: 3012
February 14, 2005 Location: Moscone West Convention Center

Session Chairs: Diana Farkas, Virginia Tech, Dept. of Matls. Sci., Blacksburg, VA 24060-0237 USA; Ju Li, Ohio State University, Dept. of Matls. Sci. & Engrg., Columbus, OH 43210 USA

2:00 PM Invited
Minimum Energy Paths of Thermal Activation at Crack Tips: Ting Zhu[2]; *Ju Li*[1]; Sidney Yip[3]; [1]Ohio State University, Dept. of Matls. Sci. & Engrg., 494 Watts Hall, 2041 College Rd., Columbus, OH 43210 USA; [2]Massachusetts Institute of Technology, Dept. of Mechl. Engrg., Cambridge, MA 02139 USA; [3]Massachusetts Institute of Technology, Dept. of Nucl. Engrg. & Dept. of Matls. Sci. & Engrg., Cambridge, MA 02139 USA

We study thermally activated processes of crack-tip dislocation emission (Cu), crack kink nucleation and migration (Si), and chemically enhanced slow crack growth (SiO2+H2O). The nudged elastic band and dimer methods, guided by mechanical insights, are implemented to explore the atomistic energy landscapes and determine the minimum energy paths (MEPs) and saddle-point energies. In Cu (PRL 93, 025503), we find at 75% of the strain energy release rate for spontaneous dislocation emission, the activation energy for 3D bow-out emission is 1.1 eV, significantly higher than the continuum estimates. This is likely due to (a) negligence of surface deformation energetics, and (b) the dislocation core energies in continuum models have not been calibrated against atomistic calculations. In Si, we compute the crack kink formation and migration energies for different crack front orientations on the (111) cleavage plane, to explain the experimentally observed crack propagation directional anisotropy. In SiO2, we compute the activation pathways of water attacking strained Si-O-Si bridge. The stress-dependent activation energies are obtained, and we have found three competing MEPs, that are rate-controlling at low, medium and high stresses, respectively.

2:35 PM
Surface Energy of Silicon Calculated by Molecular Dynamics Method: *Takashi Mizuguchi*[1]; Ken-ichi Ikeda[1]; Fuyuki Yoshida[1]; Hideharu Nakashima[1]; Hiroshi Abe[1]; [1]Kyushu University, Interdisciplinary Grad. Sch. of Engrg. Scis., kasugakoen 6-1, Kasuga, Fukuoka 816-8580 Japan

Silicon shows a sharp brittle-ductile transition and is a brittle material at room temperature. Because the surface energy is considered to affect the fracture behavior of a brittle material, it is important to investigate the surface energy just after fracture in order to clarify the details of fracture mechanism. This study was carried out to clarify systematically the crystal orientation dependence of surface energy just after fracture by molecular dynamics calculation. The surface energy after annealing at 1098K was also calculated and compared with that just after fracture. It was revealed that surface energy of (111) had the minimum value. This agrees with the fact that the cleavage plane of silicon is (111). It was also found that the surface energy after 1098K annealing was lower than that just after fracture. It is concluded that the decrease in surface energy is brought about by the rearrangement of surface atoms.

2:55 PM
Ab-Initio Based Classical Potential Describes Dislocation Motion and Solute Effects in BCC Molybdenum: *Richard G. Hennig*[1]; Dallas R. Trinkle[2]; Thomas J. Lenosky[1]; Chris Woodward[2]; John W. Wilkins[1]; [1]Ohio State University, Dept. of Physics, 174 W 18th Ave., Columbus, OH 43210 USA; [2]Air Force Research Laboratory, Wright Patterson AFB, OH 45433 USA

Molybdenum's high strength and high-temperature stability makes this refractory metal very attractive for use in advanced process technologies; however, the pure metal is very brittle. Solutes can soften molybdenum; though, a microscopic understanding is missing. To describe plastic deformation requires knowledge of how dislocations—the defects responsible for crystal plasticity—evolve under stress. An ab initio based classical potential extends the accuracy of density functional theory to the relevant length scales for dislocations. The classical potential of the modified embedded atom type accurately predicts defect energies, phonon dispersion, melting, dislocation structures and Peierls stresses of the bcc phase. The atomistic effect of solutes on the dislocation core and the Peierls stress is systematically determined as a function of solute size and modulus misfit. The results explain the experimental observations of low temperature softening by Re and hardening by Hf. Supported by DOE grant DOE-DE-FG02-99ER45795 and NSF grant NSF-FRG-739792.

3:15 PM
Atomistic Study of Screw Dislocation - Obstacle Interactions in BCC Mo: *Hyon-Jee Lee*[1]; Jae-Hyeok Shim[1]; Brian D. Wirth[1]; [1]University of California, Dept. of Nucl. Engrg., Berkeley, CA 94720-1730 USA

The effect of irradiation on materials produces large increases in strength, which are attributed to dislocation resistance from irradiation-induced point defect clusters. Large-scale molecular dynamics (MD) simulation simulations have been used to study the sequence of events controlling the interaction between screw dislocations (of 100 burgers vector length) and the commonly observed radiation obstacles such as voids or interstitial loops in body centered cubic (BCC) molybdenum. The MD simulations have been performed using a Finnis-Sinclair potential. Considering the unique non-planar core structures of BCC screw dislocation, we first report the behavior of screw dislocation motion as a function of temperatures and applied stresses. Then, we introduce defects into the system and observe their interaction behavior with screw dislocations in both dynamic and static conditions.

3:35 PM
Computer Simulation of Solute Effects on Dislocation Motion in Model Fe-Cu and Fe-C Solid Solutions: *Kanit Tapasa*[1]; David J. Bacon[1]; Yuri N. Osetsky[2]; [1]University of Liverpool, Dept. of Engrg., Brownlow Hill, Liverpool L69 3GH UK; [2]Oak Ridge National Laboratory, Computer Scis. & Math. Div., PO Box 2008, Oak Ridge, TN 37831-6158 USA

Glide of an edge dislocation in iron containing solute atoms has been investigated using atomic-scale computer simulation. Models for two different solutes types have been considered, namely substitutional copper and interstitial carbon. The influences of solute at up to 1at%Cu and 0.5at%C have been treated. The dependence of dislocation velocity on stress and temperature under dynamic conditions has been investigated and compared with similar modelling for pure iron.

In addition, the attraction and repulsion of a dislocation due to either a single solute atom near the dislocation glide plane or pairs of solutes across the glide plane have been studied in terms of the interaction energy and the resolved shear stress for glide (Peierls stress) at T = 0K. The results are discussed in relation to the dynamics of dislocation drag and predictions of dislocation-defect interactions obtained from elasticity theory.

3:55 PM Break

4:05 PM Invited
Dislocation Motion and Dislocation-Twin Interactions in Zirconium: Atomistic Modeling and Experiments: *S. G. Srinivasan*[1]; M. I. Baskes[1]; A. Misra[1]; R. J. McCabe[1]; [1]Los Alamos National Laboratory, Matls. Sci. & Tech., Los Alamos, NM 87545 USA

We will describe our recent atomistic calculations of dislocation motion and dislocation-twin interactions in hexagonally close packed zirconium metal (Zr). A semi-empirical modified embedded atom method potential that includes angular forces, describes the interactions between Zr atoms. The stresses to move basal, prism, and pyramidal edge and screw dislocations in single crystal Zr are computed as a function of temperature. We find that at low temperature the basal dislocations move much easier than the prism dislocations. The stress needed to move the prism dislocation decreases significantly at higher temperature. We also will present results on the nucleation of dislocations from Zr free-surfaces and from twin boundaries, and determine the stress needed to transmit dislocations through a twin boundary. We will relate our atomistic results to detailed electron microscopy of plastically deformed Zr.

4:40 PM
Interaction of 1/3<1120>(0001) and 1/3<1120>{1100} Edge Dislocations with Point Defect Clusters in α-Zirconium: *Roman E. Voskoboinikov*[1]; Yuri N. Osetsky[2]; David J. Bacon[1]; [1]University of Liverpool, Matls. Sci. & Engrg., Dept. of Engrg., Brownlow Hill, Liverpool, Merseyside L69 3GH UK; [2]Oak Ridge National Laboratory, PO Box 2008, MS-6138, Oak Ridge 37831 USA

Atomic-scale computer modeling has been carried out for two edge dislocations with the same Burgers vector 1/3<1120> but different glide planes, (0001) and <1100>, in the hcp structure to investigate their interaction with typical point defect clusters found in high-energy displacement cascades. The dislocation in the basal slip plane splits into two partials whereas the one in the prism plane remains undissociated. The family of self-interstitial atom defects consists of a triangular cluster, an irregular 3D cluster and glissile loops with two different shapes and orientations. The population of vacancy defects includes a prismatic and pyramidal vacancy clusters. During interaction full or partial absorbtion of point defect clusters, pinning of dislocation line by cluster or due to formation of immobile segment on the dislocation, push of cluster in the glide direction occur depending on the dislocation slip plane and cluster type. Stress-strain curves have been obtained for all the simulated cases.

5:00 PM
On the Mobility and Interactions of Twinning Disconnections in the HCP Metals: *Anna Serra*[1]; David J. Bacon[2]; Yuri N. Osetsky[3]; [1]University Polytechnic of Catalonia, Dept. Applied Math. III, Jordi Girona 1-3, Barcelona 08034 Spain; [2]University of Liverpool, Matls. Sci. & Engrg., Brownlow Hill, Liverpool L69 3GH UK; [3]Oak Ridge National Laboratory, Computer Scis. & Math. Div., PO Box 2008, Oak Ridge, TN 37831-6158 USA

Conventional simulation of the atomic structure of twin boundaries and defects such as twinning dislocations uses periodic boundary conditions along the dislocation line and fixed conditions in the other two directions, so that extensive defect motion cannot be considered. A new method has been developed to simulate a twin boundary containing a disconnection defect, i.e. a step with dislocation character, with full periodicity in the boundary plane. It may be used for investigating either the static or dynamic properties of such interfaces as the defects in them move over large distances. The method is described here and is used to investigate the motion of twinning disconnections in {10-12} and {11-22} boundaries as a function of the applied stress and temperature. In addition some processes in the boundary, such as the creation of disconnection dipoles and the creation of crystal dislocations, are investigated.

5:20 PM
Atomic-Scale Modeling of Dislocation-Stacking Fault Tetrahedra Interactions in Copper: *Yuri N. Osetsky*[1]; Roger E. Stoller[2]; David J. Bacon[3]; [1]Oak Ridge National Laboratory, Computer Scis. & Math., PO Box 2008, MS-6138, Oak Ridge, TN 37831 USA; [2]Oak Ridge National Laboratory, Metals & Ceram., PO Box 2008, MS-2008, Oak Ridge, TN 37831 USA; [3]University of Liverpool, Matls. Sci. & Engrg., Brownlow Hill, Liverpool L69 3GH UK

The present paper reports recent progress in atomic-scale dislocation dynamics achieved by exploring large-scale simulation of realistic dislocation and SFT density and SFT size for both irradiation (~2-4nm) and ageing (>10nm) conditions. We have considered gliding edge and screw dislocations with the Burgers vector ½<110> interacting with perfect SFTs of size of up to 12nm over the temperature range from 0 to 600K. A variety of different reactions have been observed, such as dislocation climb, cross-slip and formation of superjogs at the dislocation line and ledges on the SFT. These cannot be rationalized without taking into account specific atomic-scale structure of dislocations and SFTs. The atomic-scale mechanisms observed are discussed and tentative interpretation of experimental results is given.

5:40 PM
Dislocation Bypass Mechanism on Cobalt Precipitate in Copper: Atomistic Approach: *Jae-Hyeok Shim*[1]; Brian D. Wirth[1]; Hyon-Jee Lee[1]; [1]University of California, Dept. of Nucl. Engrg., Berkeley, CA 94720 USA

Large-scale molecular dynamic simulations of the interaction between dislocations (edge and screw) and precipitates in Cu-Co alloys have been performed using 3-5 million atoms. Coherent Co precipitates show different resistance to the leading and trailing Shockley partial dislocations. A temperature dependent bypass mechanism of the trailing partial dislocation is observed irrespective of the dislocation type. At low temperatures, the trailing partial bypasses with the Orowan mechanism, whereas it bypasses with the shear mechanism at high temperatures. The combination of this change in bypass mechanism and the dynamic effect due to the phonon drag explains the reported anomalous temperature dependence of the critical resolved shear stress in Cu-Co alloys. Incoherent Co precipitates show more complicated dislocation interactions and bypass. Initial interactions involve dislocation annihilation and re-nucleation at the precipitate interface accompanied by interface dislocation generation which glides into the precipitate.

Computational Thermodynamics and Phase Transformations: Materials Design and Development

Sponsored by: Electronic, Magnetic & Photonic Materials Division, Materials Processing & Manufacturing Division, Structural Materials Division, EMPMD/SMD-Chemistry & Physics of Materials Committee, MPMD-Computational Materials Science & Engineering-(Jt. ASM-MSCTS)
Program Organizers: Corbett C. Battaile, Sandia National Laboratories, Materials and Process Modeling Department, Albuquerque, NM 87185-1411 USA; Christopher Mark Wolverton, Ford Motor Company, Scientific Research Laboratory, Dearborn, MI 48121-2053 USA

Monday PM Room: 3005
February 14, 2005 Location: Moscone West Convention Center

Session Chair: Koenraad G.F. Janssens, Sandia National Laboratories, Albuquerque, NM 87111 USA

2:00 PM Invited
Computational Materials Design Applications of Thermodynamics and Phase Transformations: *Charles J. Kuehmana*[1]; [1]QuesTek Innovations LLC, 1820 Ridge Ave., Evanston, IL 60201 USA

Computational Thermodynamics and phase transformations are an essential tool for the quantitative design of advanced materials. Computational thermodynamics provides information of complex phase equilibria controlling processability as well as the underlying thermodynamic inputs for detailed microstructural evolution simulations. Precipitation simulations provide control of strengthening and grain-pinning dispersions during complex thermal and mechanical processing. Displacive phase transformation models allow control of process temperatures and mechanical behavior influenced by shear transformations. Examples of the use these modeling techniques in the design of bulk metallic glasses, ultrahigh-strength precipitation strengthened stainless steels and high-strength shape memory alloys will be reviewed. Such tools can also address robust design including scalability and intrinsic process variation as well as accelerated qualifi-

cation of materials to establish confidence in a materials minimum guaranteed properties with limited available experimental data.

2:30 PM Invited
Designing Elastic Properties of Titanium Alloys: *Shigeru Kuramoto*[1]; Hideaki Ikehata[1]; Naoyuki Nagasako[1]; Junghwan Hwang[1]; Tadahiko Furuta[1]; Kazuaki Nishino[1]; Takashi Saito[1]; [1]Toyota Central R&D Labs., Inc., Advd. Metal Lab., 41-1, Yokomichi, Nagakute, Aichi 480-1192 Japan

We utilized a result of ab initio calculations to design Gum Metal, a new multifunctional titanium alloy with low Young's modulus and high strength. Elastic constants were calculated in several Ti-X binary alloys, and elastic moduli in several orientations of single crystal and those of polycrystal were estimated to obtain a basic principle to determine a compositional limitation of the alloy with low modulus. It was revealed that computational results of Young's modulus were essentially consistent with experimental results of the binary alloys, and elastic moduli in a few orientations of single crystal were expected to be minimized at the specific alloy composition which is represented by valence electron number per atom (e/a) of 4.24. Experimental results of binary, ternary and quaternary titanium alloys also exhibited substantial dependence on e/a, and some evidences of the elastic anomaly were observed in microstructure after deformation.

3:00 PM Invited
Virtual Aluminum Castings: The Ford Experiment in Integrated Computational Materials: *John E. Allison*[1]; [1]Ford Motor Company, Rsch. & Advd. Engrg., MD 3182 Scientific Rsch. Lab., Dearborn, MI 48124-2053 USA

Integrated Computational Materials seeks to unify materials models across length and time scales and knowledge domains. It has the ability to unify analysis of manufacturing, design and materials into a holistic system. It offers a solution to the paradoxical industrial need to quickly develop durable components at the lowest possible cost. This talk will describe Virtual Aluminum Castings, the Ford experiment in Integrated Computational Materials. VAC is a comprehensive, integrated and experimentally verified suite of CAE tools for optimization of cast aluminum components and processes. Our vision is that castings will be designed and virtually cast, heat treated and tested for durability, all on a workstation long before components are fabricated. This talk will review recent progress in integrating models for the Al-Si-Cu alloys typically used in automobile engine structures, including models for phase equilibria and microsegregation, aging response, and the influence of microstructure on properties. The need for a unifying activity in computational materials science in the form of a "grand challenge" will also be outlined.

3:30 PM Break

3:40 PM Invited
Trace Element Effects on Precipitation in Al-Cu-Mg-(Ag, Si) Alloys: *Aiwu Zhu*[1]; Gary J. Shiflet[1]; Edgar A. Starke[1]; [1]University of Virginia, Matls. Scis., 116 Engr.'s Way, Charlottesville, VA 22904 USA

Metastable 2nd phases play major roles for determining the mechanical properties of age-hardenable aluminum alloys. The purpose of alloy design is to enhance the precipitation of the desired 2nd phase(s) among all the competing phases. Trace elements or impurities are the sources for clusters or segregates in the quenched solid solutions and hence control the nucleation of the coherent or semi-coherent precipitates. This talk describes application of thermodynamic and first principle calculation tools to identify those elements that are either helpful or harmful. Cluster variation method based on FCC tetrahedron approximation is employed to indicate the cluster formation in the solid solutions. The energy term is calculated using first principle total energy based on LDA/GGA and the overall cluster volume relaxation or the effect of atomic size difference is considered. This FP-CVM method, together with the quasi-chemical model based on CALPHAD databases, will be compared with 3D-AP and TEM experimental observations of cluster formation prior to the precipitation in Al-Cu-Mg-(Ag, Si) alloys.

4:10 PM Invited
Aspects of Quality Assurance in a Thermodynamic Mg Alloy Database: *Rainer Schmid-Fetzer*[1]; [1]University of Clausthal, Inst. of Metall., Robert-Koch-Str. 42, Clausthal-Zellerfeld D-38678 Germany

The thermodynamic Mg alloy database, which is an ongoing long-term development project at the University of Clausthal, currently comprises 17 components and 277 phases. Quality assurance is a major concern for such a large number of components and interactions. This requires meticulous work and scrutiny during all steps, the initial generation, extension, maintenance, and updating of the database. The set of procedures (or protocol) used for quality assurance in our Mg database will be outlined. Examples will be given on how to detect and eliminate artifacts or errors in thermodynamic descriptions and the resulting phase diagrams. Standard tests on the thermodynamic functions or parameters will be shown that are of practical use in checking consistency and plausibility. The link to key experiments will be highlighted. It is suggested that such a protocol may be useful also for other thermodynamic databases. The typical final user, applying the database to a real multicomponent material or process, will generally not have sufficient time, resources, and experience to perform the quality check himself. It is thus helpful to quantify if the database developer performed quality assurance following a standard protocol.

4:40 PM Invited
Alloy Design of Creep-Resistance Magnesium Alloys from Stacking Fault Energy Calculated by First-Principles: *Kenji Higashi*[1]; Tokuteru Uesugi[1]; [1]Osaka Prefecture University, Dept. of Metall & Matls. Sci., 1-1, Gakuen-cho, Sakai, Osaka 599-8531 Japan

The first-principles calculations apply the optimizing substitutional-alloying-elements can enhance the creep resistance of Mg-based alloys, which is estimated as the materials parameter expressed in terms of stacking fault energy (SFE), based on both macroscopic phenomenological studies and mesoscopic dislocation theory. As the results, it is demonstrated that both Y and Ca among the elements investigated in the present paper are the promising elements to improve a resistance of creep controlled by dislocation-climb in the Mg-based alloys. This work presented the alloying effect on the SFE by limited additional elements in Mg-based alloys because of less computational time. Now this work is very limited examples to demonstrate the importance of atomistic analysis of the materials characteristics. In the present paper, however, we challenged to shed light on the mechanism of creep deformation in atomic scale from the first principles.

5:10 PM Invited
Computational Crystal Structure Prediction with High-Throughput Ab Initio and Data Mining Methods: *Dane Morgan*[1]; Gerbrand Ceder[1]; Stefano Curtarolo[2]; [1]Massachusetts Institute of Technology, Matls. Sci., 77 Mass. Ave., Cambridge, MA USA; [2]Duke University, Mechl. Engrg. & Matls. Sci., 144 Hudson Hall, Box 90300, Durham, NC 27708 USA

Crystal structure prediction is an essential step in rational materials design. Unfortunately, there is no general tool for reliably predicting crystal structures of new alloys. Total energy ab initio approaches can be used to accurately compare energies of different candidate structures, but developing a manageable list of candidate structures for comparison is still very challenging. A powerful new tool to tackle this problem is "high-throughput" ab initio computation, which makes use of robust automated techniques to perform many thousands of calculations. High-throughput ab initio can be enhanced with data mining techniques, which can be used to accelerate structure prediction in new alloys. We have used high-throughput methods to calculate over 14,000 full ab initio structural optimizations on 80 intermetallic binary alloys, and implemented a novel data mining scheme that shows potential to dramatically reduce the time necessary for identify stable crystal structures in new alloys.

Converter and Fire Refining Practices: Operations and Modernization

Sponsored by: Extraction & Processing Division, EPD-Pyrometallurgy Committee
Program Organizer: Alistair G. Ross, INCO, Ltd., Canadian Smelting & Copper Business, Copper Cliff, P0M 1N0 ON Canada

Monday PM Room: 2016
February 14, 2005 Location: Moscone West Convention Center

Session Chairs: Theo Lehner, Boliden Mineral AB, Rönnskär Smelter, Skelleftehamn S 932 81 Skelleftehamn; Alistair G. Ross, Inco Ltd, Canadian Smelting & Copper Business, Copper Cliff, ON P0M 1N0 Canada

2:00 PM
The Operation and Improvements of PS Converters at Tamano Smelter: *Souichiro Tanaka*[1]; M. Hamamoto[1]; M. Hashimoto[1]; Shintaro Udo[1]; [1]Hibi Kyodo Smelting Co., Ltd., 6-1-1 Hibi Tamano, Okayama Pref. 706-8511 Japan

The Tamano Smelter of Hibi Kyodo Smelting Co. Ltd. was commissioned in 1972. Since start up, the anode production capacity has

increased from 101,000 tpy to 290,000 tpy, as a result of the application of continuous improvements at each phase of the expansion projects. The Tamano Smelter had developed several innovations, including the original coke combustion technology for Flash Smelting Furnace operations (T-FSF), and has also been able to extend the operating life of the Peirce-Smith converters. This paper will present several improvements implemented at the Tamano Smelter, and will discuss relevant P-S converter operation.

2:30 PM
Current Practices at the Converter and Anode Furnace Operations of PASAR: *Romeo Urban Pagador*[1]; Mirardo Celeste Malazarte[1]; Tomas Wilfred Gonzales[1]; [1]PASAR Corporation, Smelter Div., Leyte Industl. Dvlp. Estate, Isabel, Leyte 6539 Philippines

After privatization in 1999, PASAR Corporation initiated a plant modernization program to optimize the performance of the smelter by increasing plant availability. This initiative required operational adjustments to the converting and anode furnace procedures, to support the higher throughput in the flash furnace, while continuing to meet government environmental regulations. The major shift in production direction was to eliminate the 30-35 day maintenance shutdown every two years, and replace it with a 15-day shutdown. This paper discusses the changes implemented in the converter and anode operation that have resulted in an increase of 10% in flash furnace throughput, an 18% increase in blister output, to170 MT per cycle, and a converter campaign tonnage increase of 10%. Since privatization, PASAR has instituted a series of 'management of change' programs that have facilitated an industrial cultural change needed to achieve the company's vision, mission and strategic goals.

3:00 PM
Technical Developments and Environmental Protection with the PS Converter at the Sumitomo Toyo Smelter and Refinery: *Harumasa Kurokawa*[1]; Masaru Takebayashi[1]; Naoki Kubo[1]; Shuuji Endou[1]; [1]Toyo Smelter & Refinery, Techl. Sect., Otu 145-1, Funaya, Saijo, Ehime 793-0005 Japan

Since the initial start-up, the Toyo Smelter & Refinery has been operating in harmony with the ambient environment, and improvements have been implemented with technologies specifically developed for further protecting the environment. Toyo Smelter & Refinery is now planning to increase the copper production capacity from 280,000 tpy to 450,000 tpy, over a period of several years. In 2003, the first step of this smelter expansion and modernization plan was implemented. The production capacity of the P-S converter was increased dramatically, as it became possible to operate under a '2 hot-2 blowing' schedule. In 2005, an additional converter will be installed, in order to allow operation under a '3 hot-2 blowing' schedule. This report will describe the technical improvements on the P-S converters, as well as describe the Toyo expansion program and discuss the technologies applied to the fugitive gas collecting system.

3:30 PM Break

3:45 PM
Converter Modernization and Operational Improvement at the Pirdop Smelter: *William A. Enrico*[1]; Ivailo Vasilev[1]; Nikolai Naidenov[1]; Evgeni Marinov[1]; Dimo Kirilov[1]; [1]Umicore Med JSC, Pirdop Smelter, 2070 Pirdop Bulgaria

Umicore acquired the Pirdop Smelter in a privatization offering by the Bulgarian government in September 1997. Since that time, an investment program has been conducted to increase capacity to 225 000 tons per year of anode copper, while improving the environmental performance to meet Bulgarian and European standards. A significant part of this investment program involved reconstruction of the three Peirce-Smith converters and the associated gas handling system. During the period June, 2000 through April, 2002, converter capacity was increased, the existing water-cooled hoods were replaced, the waste heat boiler was replaced by two evaporative coolers, the dry ESP's were rebuilt and extended, and a Converter Control System (CCS) installed. From 2002 until the present, a continuous improvement of operating and environmental performance has been achieved. This paper will describe the converter reconstruction project, the operational, maintenance, and environmental improvements achieved since then and additional projects presently under consideration.

4:15 PM
Copper Concentrate Smelting in Peirce Smith Converters at Onahama Smelter: Toshiyuki Kawai[1]; *Michio Nishiwaki*[1]; Shosaku Hayashi[1]; [1]MMC, Onahama Smelter & Refinery, Onahama Japan

Copper concentrate smelting directly in P-S converters was started at Onahama Smelter in 1983. Thereafter, the tonnage of concentrate smelted through the P-S converters increased, such that by 2002, it equaled the tonnage smelted through the reverberatory furnaces. In 2003, 56% of the total copper concentrates treated at Onahama Smelter were processed directly through the P-S converters. Technical improvements are reviewed and advantages of direct smelting in P-S converters are reported.

4:45 PM
Studies of Heat Exchange within the Working Space of an Electrical Nickel Anode Refining Furnace: *V. M. Paretsky*[1]; *Andrey V. Tarasov*[1]; *G. S. Nus*[1]; [1]State Research Institute of Nonferrous Metals, State Rsch. Ctr. of Russian Federation, 13, Acad. Korolyov St., 129515, Moscow Russia

The effect of the degree of nickel oxide reduction and the reaction gas composition on the furnace productivity has been estimated by computations and the established relationship is in good agreement with the practical data obtained in the process of electric smelting at the Severonickel smelter. An increase in the reduction degree within a range of =0.65 - 0.9 results in an increase in the furnace productivity by 19% to 37% and in a decrease in the unit electric power requirement by 16% to 27% depending on the reaction gas composition. The agreement between the computed and practical data has confirmed that the decisive factor for the process of treatment of reduced nickel oxide in an electric-arc furnace under the given conditions is the specific heat absorption, which is dependent on the nickel oxide reduction degree and the reaction gas composition.

Extractive Metallurgy: Hydrometallurgy

Sponsored by: Extraction & Processing Division, EPD-Aqueous Processing Committee, EPD-Pyrometallurgy Committee, EPD-Waste Treatment & Minimization Committee
Program Organizers: Thomas P. Battle, DuPont Titanium Technologies, Wilmington, DE 19880-0352 USA; Edgar E. Vidal, Colorado School of Mines, Golden, CO 80401-1887 USA; Courtney A. Young, Montana Tech of the University of Montana, Metallurgical Engineering, Butte, MT 59701 USA

Monday PM Room: 2018
February 14, 2005 Location: Moscone West Convention Center

Session Chairs: Jim Hoffmann, James Hoffmann and Associates, Houston, TX 77242 USA; Dirk Verhulst, Altair Nanomaterials Inc., Reno, NV 89502 USA

2:00 PM
Computational Modelling of Reactive Multi-Phase Flows in Porous Media: Applications to Metals Extraction and Environmental Recovery Processes: *Mark Cross*[1]; Chris R. Bennett[1]; Diane McBride[1]; T. Nick Croft[1]; James Gebhardt[2]; [1]University of Greenwich, Ctr. for Numerical Modlg. & Process Analysis, Old Royal Naval Coll., Park Row, London SE10 9LS UK; [2]PERI, 1945 S. 1100 E., Ste. 100, Salt Lake City, UT 84106 USA

There are a number of metallurgical processes where liquid and gas containing reactants flow through a porous medium interacting in such a way as to cause the extraction of metallic components. This might happen in a leach process (as in gold or copper, for example) or in some kind of environmental recovery process on spent dumps or heaps. In either class of process, there is a challenge to develop comprehensive models that enable reliable predictions of how the process will behave over the long term. In particular, there is considerable interest in predicting the base metal and other contaminant levels in the out-flowing liquid streams from the dumps or heaps, and in the case of environmental recovery, their impact upon the local ecological system in the geographical neighbourhood. The computational modelling of these families of processes present considerable challenges to the relevant research community demanding concomitant capabilities to represent: a) The liquid flow through heterogeneous porous media structures subject to variably saturated flow conditions; b) The flow of gas through the porous structure; c) The complexity and possibly dynamically changing nature of the porous media structure, and the flow conditions of either or both the gas and liquid flows; d) The transport of reactants and products of reaction in both the liquid and gas flow; e) The interaction of the liquid and gas flows with the solid porous structure with regard to a range of chemical reactions; f) The simultaneous mass and heat transfer that occurs; g) The role of microorganisms as a catalyst for reactions. Aside from the huge amount of knowledge that must be acquired to characterise each of the above features, there is a major challenge in developing a computational modelling framework that can encompass the chemical, physical, bio-

logical, engineering and environmental features that comprise chemical reactive porous media processes, whether as industrial production or environmental recovery operations. The objective of this paper is to outline these challenges and to describe how one such framework has been developed over the last few years, which can cope with arbitrarily complex geometries and, because the computational challenges are so significant, run efficiently on high performance parallel clusters.

2:25 PM
Coupling of Electrocoagulation and Alternative Energy Sources for the Removal of Arsenic Contaminants in Water: An Environment-Friendly Materials Processing: *Jewel A. Gomes*[1]; Mehmet Kesmez[1]; Michael Weir[1]; Bonnie Ardoin[1]; Praveenkumar Daida[1]; J. R. Parga[2]; David L. Cocke[1]; [1]Lamar University, Gill Chair of Chmst. & Cheml. Engrg., PO Box 10022, Beaumont, TX 77710 USA; [2]Institute Technology of Saltillo, Dept. of Metall. & Matls. Sci., V. Caranza 2400, Saltillo Coah C.P. 25000 Mexico

Arsenic contamination of well-water in different countries has caused signs and symptoms of arsenic poisoning. Although several physico-chemical treatments are presently used for the removal of arsenic compounds from drinking water, an electrochemical treatment, electrocoagulation, is a promising processing technology and currently is the most efficient (above 99% removal) and environmentally friendly technique, particularly if combined with alternative energy sources. Wind and fuel cell technologies can be considered the most promising developmental clean power sources. We will discuss new insights into the materials processing mechanisms and show the coupling of electrocoagulation with fuel cells and simulated wind energy sources. Different electrocoagulation plate materials were considered, along varied currents from the fuel cell to produce maximum arsenic removal. Coupling these technologies will remove carcinogenic arsenic from water sources, and will exhibit efficient usage of these energy sources by producing pure water for human and agricultural consumption.

2:50 PM
The Morphology Control of Cobalt Compounds and Co3O4 Powder Produced by Homogeneous Precipitation Process: Chen Song[1]; Zhang Duo Mo[2]; Wang Li Jun[1]; Luo Yuan Hui[1]; Zhang Li[1]; [1]General Research Institute for Non-ferrous Metals, Mineral Resources, Metall. & Matls., No.2 Xin jie kou wai da jie St., Beijing 100088 China; [2]Central South University, Sch. of Metallurgl. Sci. & Engrg., Yue Lu Dist., ChangSha, Hu Nan 410083 China

The precipitation from cobalt nitrate and chloride solution in the presence of urea yield dispersed cobalt compounds with different chemical compositions and morphologies. The effects of agitation and concentration of cobalt solution and Urea on precipitation morphology were investigated experimentally. In closed systems the particles were identified as cobalt basic carbonate with needle type shape. In open system, spherical and plate-like precipitations of cobalt basic cyanate are formed. The chemical formula of cobalt compounds was confirmed. As Co(OH)0.83(CO3)0.49 Ay 0.14H2O(in tightly-capped reactor: A stands for NO3- Cl-; y[A] molecular weight<12.9) and Co(OH)0.83(NCO)XAy0.14H2O. (in open reactor A stands for: NO3-;Cl-;42x+ y[A]molecular weight<44.82). The precursor particles transform to Co3O4 on calcining. The shap of Co3O4 particle with porous character has inheritance with precipitation. The particles formation follows by the principle of nucleation-aggregation in aqueous solution. The aggregation has played an important role. During the calcine, the aggregation was destroyed partly.

3:15 PM
Precursor Synthesis of Fibrillar Nanocrystalline Nickel Powder: Wu Jian Hui[1]; *Zhang Chuan Fu*[1]; Zhan Jing[1]; Li Chang Jun[2]; Bai Meng[3]; [1]Central South University, Sch. of Metall. Sci. & Engrg., Changsha, Hunan 410083 China; [3]JiangXi Copper GuiXi Smelter HuaXin Metal Liabilities Co., Ltd, Guixi, Jiangxi 335424 China

The composition and morphology of the precursor of fibrillar nanocrystalline nickel powder prepared by oxalate precipitation are characterized by XRD, IR and SEM analysis, and the effects of temperature, nickel ion concentration, pH value, surfactant and drying process on the morphology and dispersion of the precursor are investigated in detail. The experiment results shows that fibrillar precursor is complicated nickel salt. The precursor in well dispersive and fiber can be obtained under conditions that are proposed: precipitation temperature is 60~70 C; the nickel ion concentration is 0.6~0.8 mol/L; pH value is 8.4~8.6 and addition of PVP surfactant is 0.5%wt.

3:40 PM Break

3:55 PM
The Use of Functionalized Adsorbents in the Recovery of Copper-Complexed Cyanide from Gold Leach Solutions: *Steven F. McGrath*[1]; Rainer Bauder[1]; [1]MR3 Systems, Inc., 435 Brannan St., Ste. 200, San Francisco, CA 94107 USA

The presence of copper minerals in ores that are processed by cyanide leaching for gold recovery causes numerous problems. Dissolution of copper in the leach solution parasitically consumes cyanide and oxygen, retards gold dissolution and interferes with gold recovery processes. Additionally, the presence of copper cyanide complexes in the tailings of gold mine operations is problematic because the destruction of cyanide is impeded when the molecule is complexed with metals, and it persists in the environment. Extraction of copper cyanide complexes from the leach solution and recovery of the cyanide will improve the economics of a mining operation and mitigate the environmental liability associated with having residual weak acid dissociable (WAD) cyanides in tailings. Ion exchange materials have historically been incorporated in processes designed to solve these problems. This paper presents some recent advances in applying functionalized adsorbents to assist in cyanide recovery and copper removal from cyanide leach solutions.

4:20 PM
A Novel Perspective Method for Serpentinite Treatment: *Nshan H. Zulumyan*[1]; Zaruhi H. Hovhannisyan[1]; Aghasi R. Torosyan[1]; Sona E. Ghazaryan[1]; [1]National Academy of Sciences of the Republic of Armenia, Inst. of Gen. & Inorganic Chmst., 2-tup., Argutyan St. 10, Yerevan 375051 Armenia

A novel thermal-acid method for treatment of serpentinous ultrabasic rocks has been found. It allows extract completely magnesium and iron in the form of salts, hydroxides or oxides, as well as SiO_2 in the form of aquagel. It should be noted that up to present two methods are known to prepare aquagel by sol-gel processes: a) from the soluble silicates and b) from silica compounds like to SiH_4, $SiCl_4$ or $Si(OR)_4$. The suggested method can be seen as third one. The aquagel obtained from the serpentinites has specific behavior. For example after hydrosilicagel filtration 1 mol of SiO_2 can quite stable hold more then 64 mol of water and has particles in nanosize dimensions. According to the preliminary estimations from 1 tone of rock it is possible to extract 400kg MgO, 70-80kg Fe_2O_3, 150kg SiO_2 and 300-320kg active silica fine-grained powder.

Friction Stir Welding and Processing III: High-Temperature Materials

Sponsored by: Materials Processing & Manufacturing Division, MPMD-Shaping and Forming Committee
Program Organizers: Kumar V. Jata, Air Force Research Laboratory, Materials & Manufacturing Directorate, WPAFB, OH 45433 USA; Thomas J. Lienert, Los Alamos National Laboratory, Los Alamos, NM 87545 USA; Murray W. Mahoney, Rockwell Science Center, Thousand Oaks, CA 91360 USA; Rajiv S. Mishra, University of Missouri, Metallurgical Engineering, Rolla, MO 65409-0340 USA

Monday PM — Room: Nob Hill C/D
February 14, 2005 — Location: San Francisco Marriott

Session Chair: Thomas J. Lienert, Los Alamos National Laboratory, Los Alamos, NM 87545 USA

2:00 PM Keynote
An Investigation into the Effect of Substrate Thickness and Machine Characteristics on Friction Stir Processing of Ni Al Bronze Alloy 95800: *Leo Christodoulou*[1]; William A. Palko[2]; Christian Fuller[3]; [1]DARPA/DSO, 3701 N. Fairfax Dr., Arlington, VA 22203 USA; [2]Naval Surface Warfare Center, Carderock Div., 9500 MacArthur Blvd., W. Bethesda, MD 20817 USA; [3]Rockwell Scientific, Structl. Metals, 1049 Camino Dos Rios, Thousand Oaks, CA 91360 USA

The effect of substrate thickness and equipment characteristics on the mechanical and microstructural properties of friction stir processed (FSP) cast Ni Al bronze (NAB) alloy 95800 was investigated using single-pass 0.5 inch deep FSP regions in plates ranging from 0.5 to 1.5 inches thick. Two different friction stir units were compared to determine the effect of equipment characteristics. Visual observation showed that the radiated energy generated at the tool/plate interface was different for the two FSP machines, and the average plate temperature was higher for the unit exhibiting the higher amount of radi-

ated energy. Metallographic examination showed only minor differences in the macrostructure and microstructure of the FSP zone (for a given plate size) produced by either FSP unit. However, increasing plate thickness caused an increase in strength and a reduction in tensile ductility. Methods to mitigate the loss of tensile ductility were also examined.

2:30 PM Invited
Tungsten - Rhenium Tooling for Friction Stir Welding: James Downs[1]; Todd Leonhardt[1]; *Don Mitchell*[1]; [1]Rhenium Alloys Inc., 1329 Taylor St., Elyria, OH 44036 USA

Tungsten 25% rhenium was selected due to its enhanced physical properties, which are a high modulus of elasticity, good ductility, lower ductile brittle transition temperature and a high recrystallization temperature. The initial FSW tooling has gone through a evolution in processing from producing a lower density rod with poorer properties to high density high strength FSW tool, used for applications involving the welding of thick sections of various steels and/or titanium alloys. A discussion of the processing, properties and microstructures will be presented with a review of early production of tungsten 25% rhenium rods to present tungsten-rhenium alloys.

2:50 PM
Friction Stir Welding of Nitinol: *Blair London*[1]; Jennifer Fino[2]; Alan R. Pelton[2]; Christian Fuller[3]; Murray Mahoney[3]; [1]Cal Poly State University, Matls. Engrg. Dept., San Luis Obispo, CA 93407 USA; [2]Nitinol Devices & Components, 47533 Westinghouse Dr., Fremont, CA 94539 USA; [3]Rockwell Scientific Company, 1049 Camino dos Rios, Thousand Oaks, CA 91360 USA

Nitinol, a shape-memory alloy, is difficult to fusion weld to itself and to other metals, which can make processing operations expensive and can limit applications for the alloy. Void-free friction stir welds were produced in 3 mm and 6 mm thick nitinol plates using a polycrystalline cubic boron nitride tool. The weld microstructures were documented with optical and scanning electron microscopy. The austenitic and martensitic transformation temperatures of the weld regions were measured using differential scanning calorimetry. The FSP nugget showed a slightly reduced average grain diameter (33 mm) from the base metal (43 mm). The austenite finish (Af) transformation temperature was lower in the processed region (-22.5°C) compared to the base metal (15.0°C). An important characteristic of a welded nitinol structure is its ability to undergo deformation processing. Preliminary results of hot-rolling studies on friction stir processed nitinol will be presented.

3:10 PM
Friction Stir Welding of MA 957 Oxide Dispersion Strengthened Ferritic Steel: *Bharat K. Jasthi*[1]; Stanley M. Howard[1]; William J. Arbegast[2]; Glenn J. Grant[3]; Santosh Koduri[3]; Darrell R. Herling[3]; [1]South Dakota School of Mines and Technology, Dept. of Matls. & Metallurgl. Engrg., 501 E. St. Joseph St., Rapid City, SD 57701 USA; [2]South Dakota School of Mines and Technology, Advd. Mfg. Procg. Ctr., 501 E. St. Joseph St., Rapid City, SD 57701 USA; [3]Pacific Northwest National Laboratory, Matls. Sci. Div., K2-03, 902 Battelle Blvd., Richland, WA 99352 USA

This paper describes the results of friction stir welding MA 957. This material cannot be welded by conventional means because the ferritic steel structure contains extremely fine oxide particles such as yttria that rise in the molten weld pool. In this investigation friction stir welding was used in an attempt to obviate the fusion welding difficulties. Metallographic analysis of the post friction-stir welded material was performed to determine the distribution of the oxide dispersion and the likely structural implications resulting from its disturbance during friction stir welding.

3:30 PM Break

3:50 PM Invited
FSW of Beta Titanium Alloy Sheet: *A. P. Reynolds*[1]; Elizabeth Hood[1]; [1]University of South Carolina, Dept. of Mechl. Engrg., Columbia, SC 29208 USA

Alloy Beta 21S sheet was friction stir welded over a wide range of welding parameters. Excellent weld quality and mechanical properties were observed for all conditions. The textures in all of the welds was measured by OIM. When suitably rotated, all textures correspond to standard torsion textures observed in other BCC alloys. The required rotations varied with the welding parameters. Grain misorientation distributions and weld nugget grain size were also quantified as functions of weld parameters.

4:10 PM
Interface Microstructure in Dissimilar Friction Welded Joint: *Raghavan Ayer*[1]; Russell Mueller[1]; H. Jin[1]; Shiun Ling[1]; Steven Ford[2]; [1]Corporate Research Laboratory, Exxon Rsch. & Engrg. Co., 1545 Rt. 22 E., Annandale, NJ 07920 USA; [2]ExxonMobil Upstream Research, PO Box 2189, Houston, TX 77252-2189 USA

The interface microstructure of a Fe/Ni dissimilar Friction Stir welded joint was investigated to understand the mechanism of bonding during the Friction Stir Welding (FSW) process. The microstructure of the joint was characterized in detail by transmission electron microscopy and the remnant plastic strain across the interface determined by micro x-ray line broadening. The studies revealed that although interface diffusion of the elements was limited to a 5-10 ?Ým range and the effective diffusivities were significantly enhanced by the point defects introduced by the plastic deformation during joining. The measured x-ray strain profiles were effective in delineating the various zones (e.g. heat affected zone, thermo-mechanically affected zone) during FSW. The results of the study will be presented and the implications on the FSW of high temperature materials discussed.

4:30 PM
Friction Stir Welding of Dual Phase Steel Sheets: *M. P. Miles*[1]; J. W. Pew[1]; T. W. Nelson[1]; [1]Brigham Young University, Coll. of Engrg. & Tech., 265 CTB, Provo, UT 84602 USA

Dual phase steel is a high strength sheet steel with potential for downgauging in automotive applications, compared to standard lower strength drawing quality steels. It has good formability, but its weldablity is fair. Therefore, in cases where dual phase steel sheets are joined laser welding results in high peak hardness in the weld nugget, lowering its ductility. As an alternative, friction stir welding was investigated as a possible method of joining dual phase steel sheets. Initial results indicate that the hardness in the weld nugget is less than that of laser welded sheets, which should result in better weld formability in tailored blank applications. Tension and formability testing was used to compare the performance of the laser welded sheets with friction stir welded sheets.

4:50 PM
Friction Stir Processing of Ferrous Alloys Using Induction Preheating: *Uma Ramasubramanian*[1]; Bryan Matthew Tweedy[1]; William J. Arbegast[1]; [1]South Dakota School of Mines and Technology, Advd. Matls. Procg. Ctr., 501 E. St. Joseph St., Rapid City, SD 57701 USA

The Advanced Materials Processing Center (AMP) at the South Dakota School of Mines and Technology is evaluating forces, temperature and wear on PCBN high temperature pin tools (HTP) with and without induction preheating. The objective is to show that induction preheating reduces the stresses on the pin tool thereby extending pin tool life. Friction stir plunge testing was carried out on 6.4 mm (0.25 inch) 1018 steel plates and 12.7 mm (0.50 inch) grey cast iron plates with force and temperature data collected. A friction factor with and without induction preheating is determined which can be used to assess the degree of interaction (plasticizing) between the pin tool and the flowing metal. The microstructures of the plunges were characterized and micro hardness measurements were taken across the transverse section of the weld to distinguish the different metallurgical zones and are related to maximum temperatures observed.

5:10 PM
The Effect of Friction Stir Processing on the Microstructure and Strength of Cast Ti-6Al-4V: *Mary Juhas*[1]; Paul Pavka[1]; David Norfleet[1]; Anthony P. Reynolds[2]; Jim Williams[1]; [1]Ohio State University, Coll. of Engrg., 2070 Neil Ave., Rm. 323 Hitchcock Hall, Columbus, OH 43210 USA; [2]University of South Carolina, Mechl. Engrg., 300 Main St., Rm. A127, Columbia, SC 29208 USA

The fully lamellar as-cast structure of Ti-6Al-4V is characterized by relatively low strength but high toughness and good fatigue crack growth resistance. In most Ti alloys fatigue crack initiation resistance is enhanced by higher strength, especially in the long life regime (HCF). We have used friction stir processing (FSP) to modify the surface microstructure of cast and HIPd Ti-6Al-4V slabs. FSP creates a very fine grained structure which typically has increased strength. The hypothesis is that higher flow stresses equate with better fatigue crack initiation resistance. We will describe the FSP method and show the effect of this process on the microstructure. A new technique to determine local flow stress variations is used. This technique uses a focused ion beam to create small, cylindrical pillars and a nanoindentor apparatus to compress these pillars, yielding a load displacement curve. These results will be presented and discussed. This work sponsored by ONR.

Frontiers in Solidification Science: Morphological Evolution and Mushy Zone Phenomena II

Sponsored by: Materials Processing & Manufacturing Division, MPMD-Computational Materials Science & Engineering-(Jt. ASM-MSCTS), MPMD-Solidification Committee
Program Organizers: Ralph E. Napolitano, Iowa State University, Ames Laboratory, Department of Materials Science and Engineering, Ames, IA 50011 USA; James R. Morris, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6115 USA

Monday PM Room: 2020
February 14, 2005 Location: Moscone West Convention Center

Session Chairs: Michel Rappaz, Ecole Polytechnique Federale de Lausanne, Lausanne Switzerland; Jeff J. Hoyt, Sandia National Laboratory, Albuquerque, NM 87122 USA

2:00 PM Invited
Analysis of Solidification Microstructures During Wedge-Casting: *J. H. Perepezko*[1]; K. Hildal[1]; [1]University of Wisconsin, Dept. Matls. Sci. & Engrg., 1509 Univ. Ave., Madison, WI 53706 USA

Microstructure evolution is a function of both alloy composition and solidification thermal history. With a wedge-shaped mold, castings can be subjected to a range of cooling rates differing by orders of magnitude, typically 1-1000 K/s in a single run. With proper time-temperature measurements of the quenching melt and heat transfer analysis, wedge-casting is an effective tool to explore the spectrum of alloy solidification microstructures. The applications range from a determination of the critical cooling rate for glass formation, the measurement of the carbon equivalent in cast iron or the secondary dendrite arm spacing and porosity distribution in cast aluminum alloys. A wedge-casting mold equipped with thermocouples and fiber optic sensors has been applied to the analysis of microstructure evolution and phase selection as a function of cooling rate and undercooling in a bulk glass forming Fe-Cr-B alloy.

2:35 PM Invited
Prediction of Dendrite Growth Directions: *Alain Karma*[1]; [1]Northeastern University, Dept. of Physics, Boston, MA 02139 USA

Dendrites are well-known to have preferred growth directions relative to their crystal structure. In metals with an underlying cubic symmetry, <100> directions are often, albeit not always, selected. This raises the basic question: what determines the preferred growth directions of a dendrite? The traditional answer to this question has been that these directions correspond to maxima of the interfacial energy. This answer has been widely confirmed by solvability theory and phase field simulations for the simplest case where the solid liquid gamma plot is parameterized by a single anisotropy parameter, epsilon_1, which measures the magnitude of the four fold symmetric variation of gamma in a (100) plane. In this parameterization, only <100> growth directions are possible for positive values of this parameter. Even though the interfacial energy is very weakly anisotropic in metal systems, recent molecular dynamics simulations have revealed that two anisotropy parameters turn out however to be necessary to represent the entire gamma plot, where the second parameter epsilon_2 is the coefficient of the next higher order term in a cubic harmonic expansion of the gamma plot. The above question can therefore be rephrased by asking what are the preferred dendrite growth directions in this two-dimensional parameterization (epsilon_1,epsilon_2) of the gamma plot. This talk examines the answer to this question through quantitative phase-field simulations of dendritic evolution in two and three dimensions and the extension of solvability theory to higher order gamma plots. The main conclusion is that dendrite growth directions need not always correspond to extrema of the gamma plot and hence to low index <100>, <110>, and <111> directions. Most relevant for interpreting recent experiments in Al alloys is the finding that the growth direction can vary continuously from <100> to <110> over a domain of the (epsilon_1,epsilon_2) parameter space, which encompasses observed growth directions near <320>. Existing predictions of anisotropy values from atomistic simulations for pure Al fall close to this domain, which makes the selection of experimentally observed non-<100> orientations by various alloying elements quite plausible.

3:10 PM Invited
Coarsening of Dendritic Microstructures: R. Mendoza[1]; D. Kammer[1]; K. Thornton[2]; *P. W. Voorhees*[1]; [1]Northwestern University, Matls. Sci. & Engrg., 2220 Campus Dr., Cook Hall, Evanston, IL 60208 USA; [2]University of Michigan, Matls. Sci. & Engrg., Ann Arbor, MI USA

We investigate the evolution of dendritic microstructures during coarsening using three-dimensional reconstructions and computations. We have measured the morphology of these evolving microstructures using measurements of the interfacial shape distribution, the probability of finding a patch of interface with a given pair of principle curvatures, the spatial anisotropy of the microstructure using the normals to the interfaces, and the genus of the microstructure. Three-dimensional phase field calculations are employed to follow the evolution of the interfacial shape distribution. Using the phase field calculations we compute the average time rate of change of a given pair of principle interfacial curvatures and the flux in probability space. We show that this flux predicts qualitatively the evolution of the interface shape distribution and can be used to understand the mechanisms responsible for coarsening in these topologically complex systems. A comparison between the predictions of the calculations and experiments will be given.

3:45 PM
A Statistically Significant Analysis Technique of Microsegregation in Multicomponent Alloys: *Muthiah Ganesan*[1]; David Dye[1]; Peter D. Lee[1]; [1]Imperial College London, Dept. of Matls., Exhibition Rd., London, England SW7 2AZ UK

Instrumental errors in microsegregation measurements in multicomponent alloys complicate the treatment of randomly sampled data, leading to mis-estimation of segregation parameters such as the partitioning coefficient and segregation range. A new, physically reasonable, alloy-independent data treatment algorithm is presented that is capable of separating these errors from the underlying segregation trends. In comparison to other data treatment strategies such as the Flemings-Gungor, this new approach exploits all the information in the microprobe data set and assign each measured location a unique fraction solid. Artificial tails commonly seen in the solute distribution profiles are also minimised if not eliminated, matching the expected results from a conventional Scheil analysis of solidification partitioning. Improved estimates of the dendrite tip partitioning are obtained. This new technique is applied to examine microsegregation and heat treat ability response of four successive generations of single crystal superalloys castings.

4:05 PM Break

4:15 PM Invited
Experimental Study of the Stability of Lamellar Eutectic Growth in Bulk Samples: *Gabriel Faivre*[1]; Silvere Akamatsu[1]; Sabine Bottin-Rousseau[2]; [1]CNRS, 140 rue de Lourmel, Paris France; [2]UPMC, 140 rue de Lourmel, Paris France

We shall present real-time observations of the directional-solidification microstructures of a transparent non-faceted binary eutectic alloy (CBr_4-C_2Cl_6) in bulk (100- to 500-µm-thick) samples. The two-phase growth front is observed from the top through the liquid and a wall of the glass container with a long-distance microscope. At near-eutectic concentrations, the growth pattern is essentially lamellar. The direction of the lamella plane is arbitrary at the onset of the solidification, but a preferred direction normal to the container walls is progressively established after a long time of pulling. We study the stability of the lamellar pattern as a function of the interlamellar spacing λ at a fixed pulling velocity V - or, equivalently, as a function of V at fixed λ. The lower stability limit is due to a lamella termination instability that occurs at λ˜0.7 λ_m, where $\lambda_m \sim V^{0.5}$ is the minimum-undercooling spacing (in our case, λ_m˜14 µm for V=1 µms^{-1}). The upper stability limit occurs at l˜0.85 lm, and is due to a zigzag bifurcation. The zigzag patterns are stable up to about 1.1 λ_m. Above this limit, they undergo a lamella break-up instability that leads either to a decrease of the spacing through the creation of new lamellae, or to the formation of topological line defects (phase jumps), which resemble the “line faults” that are commonly observed in the cross-sections of bulk metallic samples. Preliminary results about the competition between lamellar and rod-like patterns that takes place at off-eutectic concentrations will also be presented.

4:50 PM Invited
Morphological Stability of Lamellar and Rod Eutectic Growth: Andrea Parisi[1]; *Mathis Plapp*[1]; [1]CNRS/Ecole Polytechnique, Lab. PMC, Ecole Polytechnique, Palaiseau 91128 France

The morphological stability of lamellar and rod eutectic coupled growth is investigated by means of three-dimensional phase-field simulations, both for a generic eutectic alloy with a symmetric phase diagram and for the transparent organic alloy carbontetrabromide-hexachloroethane. The instabilities that limit stable steady-state growth at large spacings are identified for both lamellae and rods. For lamellae,

a zig-zag instability occurs, which can saturate or lead to the breakup of the lamellae into rods or labyrinth structures, depending on the initial spacing and the volume fractions. The simulation results are in good quantitative agreement with recent experimental observations. Rods undergo a shape transition with increasing spacing from circular over oval to a dumbbell-like section, followed by splitting into smaller rods or a transition to lamellae. The implications of these findings for the lamella to rod transition and the selection of the final microstructural patterns are discussed.

5:25 PM Invited
Spatio-Temporal Microstructure Evolution in Directional Solidification Processes: *Shan Liu*[1]; Jehyun Lee[2]; Rohit Trivedi[1]; [1]Iowa State University, Ames Lab.-USDOE, 235 Wilhelm Hall, Ames, IA 50010 USA; [2]Changwon National University, Dept. Metall. & Matls. Sci., Kyungnam S. Korea

Directional solidification has been extensively used to disclose the relationship between microstructure lengthscales with processing variables. Diffusion-only thermosolutal transport has usually been assumed to develop theoretical models for microstructure evolution, however this is not necessary correct for a solidification process conducted on ground. In this paper, we will explore the versatile microstructures formed in directionally solidified off-eutectic Al-Cu alloys. In a single solidification process, primary phase, rod eutectic and lamellar eutectic can grow at different parts of the growth interface due to the convective mass transfer in the bulk melt. For this spatio-temporal microstructure formation, we develop a local model which takes into account the local composition, temperature gradient, morphology and lenthscale variation and it is found that this kind of noisy microstructure can be understood if the local growth conditions can be well specified.

Frontiers in Thin Film Growth and Nanostructured Materials: A Symposium in Honor of Prof. Jagdish Narayan: Nanostructures and Nanocomposites II

Sponsored by: Electronic, Magnetic & Photonic Materials Division, EMPMD-Thin Films & Interfaces Committee
Program Organizers: N. (Ravi) M. Ravindra, New Jersey Institute of Technology, Department of Physics, Newark, NJ 07102 USA; Orin Wayne Holland, University of North Texas, Department of Physics, Denton, TX 76203 USA; Sungho Jin, University of California, Department of Materials Science, La Jolla, CA 92093 USA; Stephen J. Pennycook, Oak Ridge National Laboratory, Sold State Division, Oak Ridge, TN 37831 USA; Rajiv K. Singh, University of Texas, Austin, TX 78758-4455 USA

Monday PM Room: 3020
February 14, 2005 Location: Moscone West Convention Center

Session Chairs: Rajiv K. Singh, University of Texas, Austin, TX USA; Steve Pearton, University of Florida, Matls. Sci. & Engrg., Gainesville, FL 32611 USA

2:00 PM Invited
Aggregation Behavior of SiO2 and Al2O3 Nanopowders in Aqueous Solution With Various Ion Concentrations to Generate Dispersion-Strengthened Ni Coatings: Gabriele Vidrich[1]; *Hans Ferkel*[1]; [1]TU Clausthal, Inst. of Matls. Sci. & Tech., Agricolastr. 6, Clausthal-Zellerfeld 38678 Germany

One approach to generate nanoparticle-strengthened metal matrix material is co-deposition of metal ions and nanoparticles from metal plating baths containing dispersed nanoparticles. The aggregation behavior of the nanoparticles in the plating bath is of importance because this has a strong influence on their homogeneous distribution in the plated metal layer. Therefore, the aggregation tendency of the nanoparticles in a nickel plating bath of different nanopowder and ion concentrations as a function of the pH value was investigated by Photon correlation spectroscopy and Zeta potential measurements. An influence of the pH value on the particle aggregation can be observed, with the strongest influence close to the isoelectric point (IEP). An increasing ion concentration shifts the IEP to higher pH values. This lead to a much less pronounced compression of the particles electrolytic double layer than expected, directly influencing the Zeta potential and the aggregation behavior. The results are discussed.

2:30 PM
Synthesis of Nanostructured WC by Solid State Combustion Process: *Hyung Il Won*[1]; Hayk H. Nersisyan[1]; Chang Whan Won[1]; [1]Chungnam National University, RASOM, Daejeon, Yusong 305-764 S. Korea

A new cost-effective process to produce nanostructured WC powder has been developed. WC nanostructured powder was produced from the WO3-NaN3-C mixture by combustion synthesis (CS) method. The formation of WC nanostructured powders and the effects of processing parameters on the microstructure, phase and size of as-synthesized nanopowders were investigated in this study. The x-ray analysis that is performed to identify the phase composition of final products suggested the formation of monophase hcp-WC powder at the combustion temperature 1050-1150°C. Beyond of these condition reaction products are multiphase and contain WC, W2C and metallic W. Diffraction lines of WC phase are width, the average crystal size which is determined from the broadening of corresponding X-ray spectral peaks by Scherrer formula corresponds to 50 nm. The morphology of WC powder obtained by TEM indicates that WC particles are soft agglomerated, spherical in shape and nanometer in size (about 20-60 nm).

2:45 PM Invited
Combustion Synthesis of Transition Metals Nanoparticles: *Hayk H. Nersisyan*[1]; Chang Whan Won[1]; [1]Chungnam National University, RASOM, Daejeon, Yuseong 305-764 S. Korea

In the present work new methodology to synthesize transition metals nanopowders (W,Mo,Ta,,Ti) under the combustion mode is developed. The preparation of metal nanoparticles was performed by reduction of MexOy in the presence of alkali metal salt as a particle size controling agent (PSCA). In the hot zone of solid flame melted salt forms protective shells around of transition metal particles formed by rapid reduction of oxide and prevents them from the agglomeration and future growing. As-synthesized Me particles have a size about 20-100 nm and specific surface area 5-15 m2/g. The salt layer also gradually reduces the pyrophoric activity of metal nanoparticles and makes them handling during the processing. Unique properties such as unusually large shrinkage, and 90-95% relative density were recorded at a temperature 800-1400°C. The technology developed was tested in a pilot technological reactor and a large-scale production possibility was discovered.

3:15 PM Break

3:30 PM
Self-Lubricant Nanocomposite Coatings Deposited by Plasma Spraying: *Xinqing Ma*[1]; Tony DeCarmine[1]; Danny T. Xiao[1]; [1]Inframat Corporation, 74 Battersin Park Rd., Farmington, CT 06032 USA

Ceramic coatings have the greatest long-term growth potential for improved wear and corrosion resistances in a variety of application cases, such as diesel engine components for ships, urban buses, locomotives, earth moving vehicles, and power generating stations, and thereby have a strong economic thrush and environmental impact. In comparison to conventional ceramic coatings, nanostructured ceramic coatings like nano-Al2O3/TiO2 have demonstrated superior performance in terms of wear, erosion and corrosion as well as mechanical properties. In this work, oxide additive acting as “soft” lubricant phase was the first introduced to a nanostructured alumina/titania matrix phase for forming a self-lubricant nanocomposite coating. The nanocomposites had been fabricated into lubricant coatings with a single layer or a functionally graded structure using a plasma spray technique. Tribological test results for the nanocomposite coatings demonstrated 4 times increase in sliding wear resistance and 3-5 times increase in abrasive wear resistance in under the tested conditions. The lowest coefficient of friction of ~0.18 was measured on the nanocomposite coating with an optimal lubricant (iron oxide or iron sulfide) content in pin-on-disk test in ethanol. Based on morphologies and wear behavior analyses, the wear mechanism was proposed for the nanocomposites. The nanocomposite coatings have exhibited the advantages of cleavability, chemical stability, low friction and high wear resistance, and will have a potential for various applications that require high lubricity at ambient and elevated temperatures.

4:00 PM Invited
Nanostructured Ceramics for Medical Applications: *Roger J. Narayan*[1]; [1]Georgia Institute of Technology, Biomatls. & Bioengrg., Sch. of Matls. Sci. & Engrg., 771 Ferst Dr. NW, Atlanta, GA 30332-0245 USA

Nanostructured ceramics may possess unique capabilities for interacting with cells, proteins, or DNA. We have developed diamondlike carbon-metal nanocomposite films, hydroxyapatite nanocomposite films, and bioglass nanocomposite films using a novel multiphase target pulsed laser deposition process. Transmission electron microscopy has shown that these films possess nanoparticle or nanolayered composite structures. These films exhibit unique mechanical, wear, corro-

sion, and biological properties. Future prospects for nanostructured ceramics in medicine are described.

4:30 PM Invited
On the Nanoscale Particles of Metals and Ferrites: *Jitendra Kumar*[1]; [1]Indian Institute of Technology, Kanpur India

Nanosize particles of noble and transition metals dispersed over aluminium oxide support have been prepared by thermal evaporation under vacuum and studied by TEM with regard to their morphology, phase(s), etc. and changes that occur in vacuum, oxygen and hydrogen at elevated temperatures. These particles are shown to exhibit phase(s) corresponding to bulk or a distorted face centred cubic in case of gold and platinum in some situations. A number of phenomena observed (namely, coarsening of particles, faceting with well defined shapes, wetting of substrate, formation of oxide/hydrides and emergence of core-and-ring or torus shape particles) have been described. Evidence has been advanced to support the Ostwald ripening mechanism for growth of particles. Some recent results on the formation of specific shapes of silver particles have also been discussed. Nanosize particles of zinc substituted manganese ferrites have been synthesized by coprecipitation method and investigated for their phase(s), surface area and magnetic properties. It is shown that the products invariably correspond to single fcc phase but with the lattice parameter decreasing with increase in zinc content. BET surface area increases with zinc substitution - indicating emergence of progressively small size. The low saturation magnetization and high Curie temperature of manganese ferrite particles in comparison to respective bulk values and changes occurring in characteristics as a consequence of partial substitution of manganese with zinc are attributed to gradual decrease of particle size, cation redistribution and/or magnetic dead layer on the surface.

5:00 PM
Distribution of Metallic (Pt, Pd) Nanoparticle Catalysts in Ceramic Substrates: *M. Shamsuzzoha*[1]; Earl T. Ada[1]; R. G. Reddy[1]; [1]University of Alabama, Metallurgl. & Matls. Engrg., PO Box 870202, Tuscaloosa, AL 35487-0202 USA

Bulk platinum and palladium have been known to be chemically inert, but show remarkably high activity as catalysts when finely dispersed as nanoparticles (<10 nm) in a ceramic substrate. In this respect, we have studied the structure, morphology and distribution of these Pt and Pd nanoparticles in gadolinium-doped ceria support by TEM and XPS. The analysis results are discussed in relation to their catalytic activity in autothermal reforming of iso-octane. Prior to reforming both metallic catalysts which are highly crystalline and often twinned appear to distribute randomly in the microstructure of the ceria support. The nanoparticle size ranges between 5 - 10 nm. A special feature found on these metal-support systems was the smooth interface between the Pt or Pd metal and the ceria support. After autothermal reforming, the metal catalysts show evidences of crystalline defects as their twinned structure show gradual dissipation. The smooth metal-support interface seem to be preserved in these catalysts even after the reforming process.

5:30 PM
Ion Beam Mixing for Processing of Nanostructure Materials: *Sufian Abedrabbo*[1]; Dia-Eddin Arafah[1]; N. M. Ravindra[2]; [1]University of Jordan, Dept. of Physics, Amman 11942 Jordan; [2]New Jersey Institute of Technology, Dept. of Physics, Newark, NJ 07102 USA

The novel technique of Ion Beam Mixing (IBM) has been utilized to process various nanostructure materials and thin films for various applications. Examples include shallow alloy formation of band gap engineered Si-Ge for solar cell applications and metallic thin films deposited on semiconductors. Characterization techniques focus on structural variations due to Argon beam irradiation of a variety of fluences by Rutherford Backscattering (RBS) and shallow defects and deep trapping level states by Thermo luminescence (TL).

Functional Thin Films for Sensors: Novel Synthesis Methods and Applications of Functional Thin Films

Sponsored by: Electronic, Magnetic & Photonic Materials Division, EMPMD-Thin Films & Interfaces Committee
Program Organizers: Anis Zribi, General Electric Global Research Center, Niskayuna, NY 12309 USA; Jeffrey Fortin, GE Global Research, Niskayuna, NY 12309 USA; Seung H. Kang, Agere Systems, Device and Module R&D, Allentown, PA 18109 USA; Choong-Un Kim, University of Texas, Materials Science and Engineering, Arlington, TX 76019 USA; N. (Ravi) M. Ravindra, New Jersey Institute of Technology, Department of Physics, Newark, NJ 07102 USA; Gerald Schultz, GE Infrastructure, Sensing, Wilmington, MA 01887-4498 USA

Monday PM — Room: 3022
February 14, 2005 — Location: Moscone West Convention Center

Session Chairs: Jeffrey Fortin, GE Global Research, Micro & Nano Struct., Niskayuna, NY 12309 USA; Seung H. Kang, Agere Systems, Device & Module R&D, Allentown, PA 18109 USA; Gerald Schultz, GE Infrastructure, Sensing, Wilmington, MA 01887-4498 USA

2:00 PM
Surface and Bulk Passivation Layer of Silicon Nitride for Solar Cell Applications: *Chuan Li*[1]; Bhushan Sopori[1]; N. M. Ravindra[2]; [1]National Renewable Energy Laboratory, Golden, CO 80401 USA; [2]New Jersey Institute of Technology, Dept. of Physics, Newark, NJ 07102 USA

It is well known that silicon nitride layers, particularly films deposited by plasma-enhanced chemical vapor deposition (PECVD), are not only useful antireflection (AR) coatings for Si solar cells, but also can serve other functions in Si solar cell fabrication. In this study, the surface and bulk passivation effects by PECVD hydrogenated silicon nitride (SiN: H) layers will be presented. Model calculations of the surface recombination velocities at the Si-SiN interface on wafers coated with nitrides deposited by various techniques are presented and discussed. A complete model of H "storage" during nitridation and its subsequent diffusion into the bulk of the Si is established and employed to explain the bulk passivation effect after nitridation. Optimization of the nitridation technique is also suggested.

2:25 PM Invited
Building Selectivity and Sensitivity in High Temperature Gas Sensors: *Prabir K. Dutta*[1]; [1]Ohio State University, 120 W 18th Ave., Columbus, OH 43085 USA

The change in resistance of semiconducting metal oxides upon exposure to gases is the basis for many gas sensors. Additives are often added to modify the chemical reactivity on the metal oxide surface. However, as the temperatures at which the sensing reactions are carried out increases, there is the possibility that the additive can also interact with the metal oxide and alter its electrical properties. We have considered several strategies for increasing sensitivity and selectivity. We have examined sputtered films of titania for sensing of carbon monoxide (CO) at 550°C. Film thickness was varied from 24-1000 nm by varying the sputtering time. The films were amorphous as prepared and converted to rutile upon thermal treatment. Highest sensor sensitivity, as measured by the resistance change of the film upon exposure to CO was noted for the ~240 nm film, and characterization focused on this film. A strategy will be presented for determining total NOx (NO + NO2) in gas streams at temperatures greater than 400°C. By using a Pt-loaded zeolite Y as a catalyst filter bed placed before a sensor, NOx species in the gas stream are brought to an equilibrium concentration of NO and NO2 that is determined by the background oxygen concentration and the filter temperature. The equilibrated NOx is then measured with a yttria stabilized zirconia (YSZ) sensor using a chromium oxide sensing electrode. This design provides the opportunity for miniaturization as well as removes the need for an air reference. We have also developed a novel Pt-zeolite filter-TiO2 sensor that responds selectively to hydrocarbons in the presence of CO. We propose that the response to propane is from the water that is liberated as a result of the oxidation reaction, and this hypothesis is based on the observation that the resistance of TiO2 at temperatures of 500-600°C decreases upon exposure to water vapor.

2:50 PM
Fabrication and Characterization of Small AFM Cantilevers Using Silicon Carbide Thin Films: Moon Jong Seok[1]; Jee Hae Geun[1]; Hyun Jae Seong[1]; Park Jin Ho[1]; *Moon Ok Min*[1]; Kim Seong

Hyun[3]; Choi Young Jin[3]; Park Jeong Ho[2]; Lee Nae Eung[2]; Boo Jin Hyo[1]; [1]Sungkyunkwan University, Chmst., 300, Chunchun-Dong, Jangan-Gu, Suwon 440-746 Korea; [2]Sungkyunkwan University, Matls. Engrg., 300, Chunchun-Dong, Jangan-Gu, Suwon 440-746 Korea; [3]Korea Electronics Technology Institute, 455-6, Masan-Ri, Jinui-Myun, Pyungtaek 451-865 Korea

We have designed and tested small AFM cantilever by using silicon carbide thin films. This work reports the application of high quality silicon carbide thin films grown by metal-organic chemical vapor deposition (MOCVD) method using single molecular precursors for micro-electro-mechanical systems (MEMS) applications. In this study, we have used and compared three kinds of the precursor molecules such as diethylmethylsilane(DEMS), 1,3-disilabutane(DSB) and tetramethylsilane(TMS) in this study. After these silicon carbide thin films were grown under most suitable condition, we tried to fabricate the AFM cantilevers using standard microfabrication processes, and then to operated it with conventional AFM equipment to characterize it. We studied their superior mechanical properties by comparing both Si and Si3N4 cantilevers. The cantilevers are 200-500§¬ thick, 5-10micron wide and 10-50micron long. Tips were grown on the cantilevers by electron-beam deposition method.

3:05 PM Invited
Design and Optimization of Polymeric Sensor Materials Using Combinatorial Chemistry Tools: *R. A. Potyrailo*[1]; [1]Biosciences, Combichemistry and Characterization Technologies, GE Global Rsch. Ctr., One Rsch. Cir., Niskayuna, NY 12309 USA

Abstract not available.

3:30 PM Break

3:50 PM Invited
New Sensing Materials and Devices: *Omowunmi A. Sadik*[1]; [1]SUNY at Binghamton, Dept. of Chmst., PO Box 6016, Binghamton, NY 13902 USA

The development of new electrode materials has expanded the range and classes of detectable compounds using electroanalytical methods. Conducting electroactive polymers (CEPs) have been demonstrated to have remarkable sensing applications through their ability to be reversibly oxidized or reduced by applying electrical potentials. For sensing applications, new approaches are required to synthesize CEPs that can combine the role of matrix immobilization template with signal generation. We have reported the synthesis of polyamic acid (PAAs) and the subsequent application of the polymers for sensor fabrication. This presentation will focus on the correlation of the electrochemical behavior of precursors (dianhydride and diamine compounds) with electrodeposition of PAA. The properties of the PAAs layers have been studied by cyclic voltammetry, scanning electron microscopy and FTIR. We will also discuss the development of a new class of polymer-stabilized metal nanoparticles using polyamic acid, polyoxydianilines and polyimides. Novel applications for sensing and metal removal will be discussed.

4:15 PM
Novel Electrospun Mesoporous Nanofibers for Gas Sensing Applications: *Rashmi Rao*[1]; Duraiswamy Srinivasan[1]; Anis Zribi[1]; [1]General Electric, Global Rsch. Ctr., Niskayuna, NY 12309 USA

Abstract not available.

4:40 PM
Designing Nanostructures for Sensor Applications: *Yiping Zhao*[1]; [1]University of Georgia, Physics & Astron., Athens, GA 30602 USA

Nanostructured materials have shown great potential in improving the sensitivity and reliability of chemical and biological sensors. The ability to control the geometric shape (size, separation, orientation, alignment, etc.) of nanostructures, and to integrate nanostructures from different materials becomes one of the great challenges for sensor fabrication. Here, I want to discuss a simple physical vapor deposition technique that could help to overcome this barrier. This so-called glancing angle deposition technique can fabricate well-aligned three-dimensional nanostructures through computer programming. By rotating the substrate in both polar and azimuthal directions, one can fabricate desired nanostructures, such as nano-rod arrays with different shapes, nano-spring arrays, and even multilayer nanostructures. This method offers full three-dimensional control of the nanostructure with the additional capability of self-alignment. There is almost no limitation on materials that can be fabricated into desired nanostructures. I will discuss the current status of the glancing angle deposition technology, its potential applications in sensor development, and its future challenges.

General Abstract Session: Composites and Coatings

Sponsored by: TMS
Program Organizers: Thomas R. Bieler, Michigan State University, Department of Chemical Engineering and Materials Science, East Lansing, MI 48824-1226 USA; John J. Chen, University of Auckland, Department of Chemical & Materials Engineering, Auckland 00160 New Zealand; James C. Earthman, University of California, Department of Chemical and Materials Science, Irvine, CA 92697-2575 USA

Monday PM Room: 2011
February 14, 2005 Location: Moscone West Convention Center

Session Chair: Mark L. Weaver, University of Alabama, Dept. of Metallurgl. & Matls. Engrg., Tuscaloosa, AL 35487-0202 USA

2:00 PM
Reaction Products of Al/TiC Composites Fabricated by Pressureless Infiltration Technique: *Kon Bae Lee*[1]; Hoon Kwon[1]; [1]Kookmin University, Sch. of Advd. Matls. Engrg., 861-1, Jongnung-dong, Songbuk-ku, Seoul 136-702 Korea

The interfacial reaction products in a 5052 Al/TiCp composite fabricated by the pressureless infiltration method were analyzed using SEM, EDS, and TEM. Since the spontaneous infiltration of molten Al-Mg alloys into the powder bed containing TiC particles occurred at 800 C for 1 hour under a nitrogen atmosphere, it was possible to fabricate 5052 Al alloy matrix composites reinforced with TiC particles. During fabrication of composites, reaction products of various morphology and size were formed in the Al matrix as well as in the vicinity of the TiC particles by the interfacial reaction between the Al alloy and the TiC particles. From the EDS and SADP analysis, it could be identifid that Al4C3, Al18Ti2Mg3, Ti2AlC, Al3Ti and TiAl were formed as interfacial reaction products.

2:25 PM
Kinetics Process of Aluminium Alloy Infiltrated the Cenosphere Particle: *L. L. Wu*[1]; G. C. Yao[1]; Y. H. Liu[1]; T. J. Luo[1]; [1]Northeastern University, Grad. Student of Sch. of Matl. & Metall., Liaoning, Shenyang 110004 China

Scanning electron microscope analysis of cenosphere fly ash reinforcement aluminium alloy composites showed that along with the increasing of heat preservation time, the quantity of cenosphere fly ash that the aluminium alloy infiltrated increased gradually. Aluminium alloy going into the cenosphere fly ash had followed two kinds of circumstances. First, aluminium alloy by way of the eyelet on particle wall entered the inside of cenosphere fly ash, and reacted with the air that present in the grain. Reduction of pressure in the interior of the grain caused molten aluminium to permeate into the cenosphere fly ash. If the particle was pressurized, aluminium alloy reacted with the oxide on the outside wall first. Due to the volume difference between the reactant and the product, hole on the airproof wall was formed. The grain had vacuum inside and made the aluminium alloy permeate inside the particle to form uniformity composite.

2:50 PM
The Production of TiC Reinforced Aluminium Matrix Composites by Elemental Carbon Addition: *I. Kerti*[1]; [1]Yildiz Technical University, Dept. of Metall. Matl. Engrg., Istanbul Turkey

Nowadays, with the highly developing modern technology, the interest on and the usage of metal matrix composites have been constantly increasing because of their properties that are much better than conventional materials. Discontinuously reinforced aluminium-based metal matrix composites (MMCS) are canditate materials for applications in the automotive, transportation, aerocpace, construction industries, because of their low density, high strength, elastic modulus, fatigue strength, wear resistance and low thermal expansion. A new production method of TiC reinforced aluminium matrix composite is the addition of elemental carbon into Al-Ti liquid phase. In this method, graphite and amorf carbon ore used as elemental carbon. The dissolved or the solid state carbon in Al-Ti alloys, react with the dissolved Ti and produce a thin reinforced phase of TiC in the molten state matrix alloy. The adventages of this method over the other are practicaly easy production, requiring no advanced technology, low cast of production, no wetting problems encountered in conventional composite materials production techniques, no impurity problems between matrix-reinforced phase interface which effects mechanical prop-

erties negatiely and shorter production time which is the most importent one of all.

3:15 PM
Influence of Deposition Parameters on the Microstructures and Properties of Ti-Cr-Al-N Based Overlay Coatings: *G. Mark Calhoun*[1]; Feng Huang[1]; Mark L. Weaver[1]; [1]University of Alabama, Metallurgl. & Matls. Engrg., Box 870202, Tuscaloosa, AL 35487-0202 USA

Recent research efforts have established that Ti-Cr-Al-N based alloys offer the potential for extending the operating temperatures of structural titanium aluminide intermetallics such as Ti-48Al-2Cr-2Nb in excess of 800°C. The present study addresses the influences of deposition parameters the microstructures, mechanical properties, and oxidation resistance of Ti-Cr-Al-N overlay coatings deposited via direct current (DC) magnetron sputtering. Coatings deposited without substrate heating were found to be amorphous when nitrogen flow ratios were maintained below 8% whereas crystalline coatings consisting of Ti and Cr-based nitrides were observed at higher nitrogen flow ratios.

3:40 PM Break

4:00 PM
Low Percolation Threshold Composites Consisting of PMMA and Carbon Black: Runqing Ou[1]; Sidhartha Gupta[1]; Charles Aaron Parker[1]; *Rosario A. Gerhardt*[1]; [1]Georgia Institute of Technology, Sch. of Matls. Sci. & Engrg., Atlanta, GA 30332-0245 USA

A conductive filler is normally added to an insulating polymer to render conductivity to the composite in applications like electromagnetic interference shielding and electrostatic dissipation. Since the filler is usually the more expensive component, it is advantageous to lower the percolation threshold. In this study, a low percolation threshold of 0.4 % vol. was achieved in PMMA/carbon black nano-composites. These composites were fabricated using a procedure involving mechanical mixing and compression molding. The average size of the CB nano-particles used was 21 nm with a DBPA of 175 ml/100g. SEM images of the composites reveal a pseudo-crystalline structure, where PMMA constitutes the pseudo-crystal grains and carbon black forms an interconnected network at the grain boundaries. The electrical properties of these composites as well as the composites made by solution mixing were determined by ac impedance measurements. It was found that the new method lowers the percolation threshold significantly.

4:25 PM
Investigation of the Effects of Fatty Acids on the Compressive Strength of the Concrete and the Grindability of the Cement: Ali Tugrul Albayrak[1]; *Muzaffer Yasar*[1]; M. Ali Gurkaynak[1]; Ismet Gurgey[1]; [1]University of Istanbul, Dept. of Chem. Engrg., Avcilar, Istanbul 34850 Turkey

In cement industry, a great energy consumption has been observed during grinding of clinker. Nowadays, to reduce this consumption, some waste products, which don't have economic utility, have been used as grinding aids. In this investigation, we have examined the effects of sunflower oil (SO), oleic acid (OA), stearic acid (SA), myristic acid (MA) and lauric acid (LA) on the fineness and strength of the cement have been examined. These aids were added into clinker in certain ratios based on the cement clinker weight and the grinding has been done for a definite time at the same condition. The results obtained were as follows: All of the fatty acids used increased the fineness as compared with the cement without the grinding additives. SO and OA decreased the strength significantly, LA decreased it to a lesser extent and SA increased it definitely according to the common cement. But MA didn't alter the strength of the cement as much as SA. Also the covering of the balls influences the grinding of cement clinker unfavourably.

4:50 PM
Electromechanical Response of Piezoelectric Composite Materials: *Ronit Kar Gupta*[1]; T. A. Venkatesh[1]; [1]Tulane University, Mechl. Engrg., 400 Lindy Boggs Ctr., New Orleans, LA 70118 USA

Recognizing the potential for the use of piezoelectric materials in a number of applications as sensors and actuators, there has been a continuing research and development effort to synthesize monolithic materials with enhanced coupled properties. Because the sensing or actuating actions of monolithic piezoelectric materials are limited, the composite approach to piezoelectric materials provides a unique opportunity to access a new design space with optimal mechanical and coupled characteristics, hitherto inaccessible through monolithic materials. Through finite-element based numerical modeling, a systematic methodology for predicting a complete set of coupled properties of the piezoelectric composites as a function of the poling characteristics, size, shape, and distribution of the constituent phases are obtained. Furthermore, a general method towards characterizing the coupled constitutive response of composite materials is also identified. Model predictions are compared with experimental results for a number of polymer-based and ceramic-based piezoelectric composites.

5:15 PM
Influence of an Organic Interlayer on the Tribomechanical Behavior of TiN Thin Films: *Patrick Jonathon Henry*[1]; Shelby Shuler[2]; Mark L. Weaver[1]; Shane Street[2]; [1]University of Alabama, Metallurgl. & Matls. Engrg., Box 870202, Tuscaloosa, AL 35487-0202 USA; [2]University of Alabama, Dept. of Chmst., Tuscaloosa, AL 35487 USA

Previously we have shown that the incorporation of dendrimer self-assembled monolayers (SAMs) can increase adhesion between metallic films to silicon-based substrates. This study centers on the influence of a dendrimer SAMs on the tribological response of TiN-based films. TiN films have been deposited via reactive DC magnetron sputtering onto SAM containing and SAM-free glass substrates using varying sputtering conditions (i.e., power, working gas pressure, and N/Ar mixture). The resulting microstructures and tribological properties are reported and discussed relative to prior observations for metallic thin films.

Hume-Rothery Symposium: The Science of Complex Alloys

Sponsored by: Electronic, Magnetic & Photonic Materials Division, EMPMD/SMD-Alloy Phases Committee
Program Organizers: Patrice E.A. Turchi, Lawrence Livermore National Laboratory, Chemistry & Materials Science, Livermore, CA 94551 USA; Thaddeus B. Massalski, Carnegie Mellon University, Department of Materials Science and Engineering, Pittsburgh, PA 15213 USA

Monday PM
February 14, 2005
Room: 3008
Location: Moscone West Convention Center

Session Chairs: Uwe Köster, University of Dortmund, Dept. of Biocheml. & Cheml. Engrg., Dortmund 44221 Germany; Tsutomu Ishimasa, Hokkaido University, Div. of Applied Physics, Sapporo 060-8628 Japan

2:00 PM Invited
Influence of Local Structure and Alloy Composition on Glass Formation and Stability: *Kenneth Franklin Kelton*[1]; [1]Washington University, Dept. of Physics, Campus Box 1105, One Brookings Dr., St. Louis, MO 63130 USA

The icosahedral quasicrysal (i-phase) is the primary crystallizing phase in a growing number of glasses. In many cases, a nanoscale microstructure is observed, likely reflecting a low nucleation barrier due to the presumed icosahedral short-range order in undercooled metallic liquids and glasses. Our recent x-ray diffraction data from electrostatically levitated metals and alloys, which support this conclusion, are presented and discussed. Since many glasses do not form quasicrystals, however, but frequently develop a similar devitrified nanostructure, other crystallization processes must be in competition. In many cases, the compositions of the amorphous and devitrified phase are different, making diffusion effects also important. The consequences of the structures of the glass and liquid and of diffusion-limited nucleation on glass formation and stability are discussed. Supported by NASA under contract NAG 8-1682, and by the NSF under grant DMR 03-07410.

2:30 PM Invited
Electronic Structure Based Approaches to Metallic Glass Stability: *Donald M. Nicholson*[1]; [1]Oak Ridge National Laboratory, CSMD, One Bethel Valley Rd., MS 6164, Bldg. 5700, Oak Ridge, TN 37830 USA

At least three factors make the determination of the electronic structure of metallic glasses difficult. First, the structure is not known from experiment; in the best circumstances only the density and pair correlations are known. Second, there is no periodicity and hence no simplifying Bloch theorem. Third, the amount of computer time required to model the electronic structure as the liquid is cooled through the glass transition is unattainable. Here, efforts to calculate the electronic structure over the past thirty years will be discussed; these include nearly free electron, effective medium, and supper cell approaches. The importance of the calculated stability of competing

crystalline phases will also be emphasized. Finally, progress in using electronic structure based forces and energies to construct classical force fields will be demonstrated by determination of the glass transition temperature and evaluation electronic, magnetic, structural, and kinetic properties of the resulting glass.

3:00 PM Break

3:20 PM Invited
Characteristic Local Structures of Bulk Metallic Glasses: *Eiichiro Matsubara*[1]; [1]Tohoku University, IMR, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577 Japan

Bulk metallic glasses (BMGs) show a clear glass transition and a large temperature span of supercooled liquid region more than 50K. In order to distinguish these new amorphous alloys from the conventional ones, they are often called bulk amorphous alloys or BMGs. Inoue introduced three guiding principles for formation of BMG, i.e. the multicomponent systems, the atomic size difference between the constituents, and the large negative heat of mixings between them. We have studied atomic structures of various BMGs, such as Zr-, Pd- and Fe-based systems by x-ray diffraction techniques. We discussed characteristics of local atomic structures in contrast with those for the conventional amorphous alloys in order to understand the origin of their structural stability. In the presentation, I will summarize these structural studies of BMGs, including the recent results on the structures of BMGs in the medium-range region by our collaborative research with the groups by electron and neutron diffractions.

3:50 PM Invited
Formability of Bulk Metallic Glasses: *Takeshi Egami*[1]; [1]University of Tennessee/Oak Ridge National Laboratory, MSE/Physics, 208 S. College, 1413 Circle Dr., Knoxville, TN 37996 USA

The glass formability depends critically upon alloy composition, and it has been known that the atomic size plays a major role. Earlier we developed a theory of glass formability based upon the atomic size ratio and the atomic level stresses such atomic size mismatch creates, which explained very well the composition limit for glass formation for binary glasses. However, recent development of bulk metallic glasses challenged this theory, which did not address the question of ease of glass formation that differentiates bulk metallic glasses from regular metallic glasses. We have extended the theory and explained the difference in the ease of glass formation, based upon the concept of distributed local glass transition and the complexity of the competing crystalline phase. It should be emphasized that this theory focuses on kinetics, not energetics, in contrast to the Hume-Rothery rules. However, there is a subtle connection, which we will discuss.

4:20 PM Invited
An Atomic Structural Model for Metallic Glasses: *Daniel B. Miracle*[1]; [1]Air Force Research Laboratory, AFRL/MLLM, 2230 Tenth St., Wright-Patterson AFB, OH 45433 USA

An atomic structural model for metallic glasses has very recently been established. Using relative atomic sizes as the primary variable, this structural model is derived from the requirement to efficiently fill space in a system of unequal spheres. Three separate comparisons with experimental data have been conducted to validate this model. The first is comparison with partial radial distribution functions, the second is with atomic coordination numbers, and the third is a prediction of metallic glass constitution. The agreement between experiment and predictions is good in all three cases, including a compelling ability to explain the compositions in a wide range of simple and complex glasses based on Zr, Pd, rare earth metals, Al, Mg and Fe. The basic features of this model will be described and the specific atomic arrangements that provide the ability to stabilize metallic glasses will be discussed. Insights gained from this model will be explored.

4:50 PM Invited
Structural Origin of the Stability of Pd-Ni-P Model Bulk Metallic Glasses Against Crystallization: *Faisal M. Alamgir*[1]; Himanshu Jain[2]; David B. Williams[2]; [1]Brookhaven National Laboratory & Hunter College, Physics Dept., 695 Park Ave., New York, NY 10021 USA; [2]Lehigh University, Dept. Matls. Sci. & Engrg., 5 E Packer Ave., Bethlehem, PA 18015 USA

The fundamental origins of the stability of the $(Pd\text{-}Ni)_{80}P_{20}$ bulk metallic glasses (BMGs), a prototype for a whole class of BMGs, were explored. While many properties of these BMGs have been characterized, their stability against crystallization has not been understood in terms of the basic structure. Therefore, we have investigated the crystallization behavior in the $(Pd\text{-}Ni)_{80}P_{20}$ glass system from the atomic and electronic structural perspective, using X-ray photoelectron spectroscopy and X-ray absorption spectroscopy, respectively. We find that the $Pd_{60}Ni_{20}P_{20}$ glass, which loosely marks the Pd-rich end of BMG formation, is stabilized through a low enthalpy component to the Gibbs free energy. The $Pd_{30}Ni_{50}P_{20}$ glass, which is near the Ni-rich end of BMG formation, is stabilized due to a large entropic cost for crystallization. The $Pd_{40}Ni_{40}P_{20}$ glass, the best glass former in the compositional range, receives stability from the kinetic hindrances imposed by having to create both a Ni-rich as well as a Pd-rich phase close to the compositions of Ni_3P and Pd_3P.

Lead Free Solder Implementation: Reliability, Alloy Development, New Technology: Intermetallic Growth in Lead-Free Solder Joints

Sponsored by: Electronic, Magnetic & Photonic Materials Division, EMPMD-Electronic Packaging and Interconnection Materials Committee
Program Organizers: Mark A. Palmer, Kettering University, IMEB, Flint, MI 48504-4898 USA; Srinivas Chada, Jabil Circuit, Inc., FAR Lab/Advanced Manufacturing Technology, St. Petersburg, FL 33716 USA; Nikhilesh Chawla, Arizona State University, Department of Chemical and Materials Engineering, Ira A. Fulton School of Engineering, Tempe, AZ 85287-6006 USA; Sinn-Wen Chen, National Tsing-Hua University, Department of Chemical Engineering, Hsinchu 300 Taiwan; Sung K. Kang, IBM, T. J. Watson Research Center, Yorktown Heights, NY 10598 USA; J. P. Lucas, Michigan State University, Chemical Engineering and Materials Science, East Lansing, MI 48824 USA; Laura J. Turbini, University of Toronto, Center for Microelectronic Assembly & Packaging, Toronto, ON M5S 3E4 Canada

Monday PM — Room: 3014
February 14, 2005 — Location: Moscone West Convention Center

Session Chairs: Sung K. Kang, IBM T.J. Watson Research Center, Microelect. Pkgg. Tech., Yorktown Hgts., NY 10598 USA; Darrel R. Frear, Freescale Semiconductor, Tempe, AZ 85284 USA

2:00 PM
A Reliability Issue for Pb-Free Solder Joint Miniaturisation: *Zhiheng Huang*[1]; Paul Conway[1]; Changqing Liu[1]; *Rachel Thomson*[2]; [1]Loughborough University, Wolfson Sch. of Mechl. & Mfg. Engrg., Loughborough, Leicestershire LE11 3TU UK; [2]Loughborough University, Inst. of Polymer Tech. & Matls. Engrg., Loughborough, Leicestershire LE11 3TU UK

As solder joints become increasingly miniaturised to meet the severe demands for future electronic packaging, it is vitally important to answer the question as to whether the solder joint size and geometry could become a reliability issue and therefore affect the implementation of the Pb-free solders. In this study, different sizes of copper bond pads are formed by depositing a copper seed layer onto silicon wafer, followed by definition of the pads through a photolithographic process with a spin-coated photoresist and subsequent electroplating to build-up the copper thickness. Different sizes of Sn-3.5(wt.%)Ag solder bumps and microstructure formed by solder dipping for different times are presented and compared. A two-dimensional thermodynamic-kinetic model is developed to assist the understanding of the kinetics of the interdiffusion and the formation of interfacial intermetallic compounds. The experimental results and theoretical predictions suggest that the solder bump size and geometry can influence the as-soldered microstructure, and therefore this factor should be taken into consideration for the design of future reliable untrafine Pb-free solder joints.

2:30 PM
Effect of Solder Composition on Morphology and Size Distribution of Cu_6Sn_5 Intermetallic Compound Grains in Reactions Between SnPb Solder and Cu: *Jong-ook Suh*[1]; Andriy M. Gusak[2]; King-Ning Tu[1]; [1]University of California, Matls. Sci. & Engrg., 6532 Boelter Hall, 405 Hilgard Ave., Box 951595, Los Angeles, CA 90095-1595 USA; [2]Cherkasy State University, Theoretical Physics, Cherkasy Ukraine

During the soldering reaction between molten SnPb and Cu, scallop-type Cu_6Sn_5 intermetallic compound grains form at the interface. By varying the solder composition from the eutectic point, we observe a change of the morphology of scallops from rounded grains to facetted grains. When molten pure Sn reacts with Cu, the Cu_6Sn_5 grains are highly facetted. Ripening of the interfacial intermetallic compound was also investigated, and size distribution and average size change were measured as a function of time. These experimental data were

compared with the kinetic model proposed in our previous study. (Phys. Rev. B66, 115403, 2002). The result showed that the average radius of intermetallic compound scallops follows $t^{1/3}$ dependence. Size distribution was also in good agreement with the proposed kinetic model.

2:50 PM
Effect of Cu Additives on Sn Whisker Formation of Sn(Cu) Finishes: *Hui-Ju Kao*[1]; Wen-Cheng Wu[2]; S. T. Tsai[2]; Cheng-Yi Liu[1]; [1]National Central University, Cheml. & Matls. Engrg., No. 300, Jungda Rd., Jhong-li, Taoyuan 320 Taiwan; [2]Yageo Corporation Nantze Branch, 16, W. 3rd St., Kaohsiung 811 Taiwan

Due to the Pb-free solder implementation, pure Sn and Sn(Cu) finishes on lead-frame and metal terminals of passive devices are commonly used. During a period of storage at room temperature, Sn whiskers were found to form on the surface of Sn(Cu) finishes, which causes serious reliability issues. In this study, we have investigated the effect of Cu additives on the Sn whisker formation of Sn(Cu) finishes. Four different Sn(Cu) finishes were studied, which were pure Sn, Sn0.7Cu, Sn1.0Cu, and Sn3.0Cu. According to the preliminary results, we found that Sn whisker formation was retarded by increasing Cu content in Sn(Cu) metal finishes. Also, we found that the density of Sn whisker formation deceased with increasing of thickness of Sn(Cu) finish layer. In this talk, we will report the detail mechanism of alloying and thickness effects on the Sn whisker formation. Also, how does the interfacial reaction between Sn(Cu) finishes and Cu substrates affect Sn whisker formation will be discussed as well.

3:10 PM
Nanoindentation of Intermetallics Formed in Pb-Free Solder Joints: Experiments and Simulation: *Xin Deng*[1]; Mark Koopman[2]; Nik Chawla[1]; Krishan K. Chawla[2]; [1]Arizona State University, Dept. of Cheml. & Matls. Engrg., Fulton Sch. of Engrg., Tempe, AZ 85287-6006 USA; [2]University of Alabama, Dept. of Matls. Sci. & Engrg., Birmingham, AL 35209 USA

A knowledge of the elastic properties of Cu and Ag-based intermetallics, formed during reflow of Sn-rich solder joints on Cu, is extremely important in understanding and predicting the mechanical behavior of the joint. Bulk testing of these intermetallics is problematic because of the difficulty in achieving fully-dense materials, and because the microstructure in bulk form is often quite different from that observed in the joint. In this study, we have used nanoindentation to probe the mechanical properties of intermetallics in the joint in situ. The Continuous Stiffness Method (CSM) was used during indentation to obtain the instantaneous Young's modulus as a function of depth. The Young's moduli of Cu6Sn5, Cu3Sn, Ag3Sn, Sn-Ag solder, pure Sn, and Cu, were measured by nanoindentation. After indentation, the surface characteristics of each phase were examined using atomic force microscopy (AFM). Significant dislocation pile-up was observed in Sn, Sn-Ag solder, and Cu. The texture of intermetallics, which has a significant effect on the elastic/plastic properties, was evaluated by Orientation Imaging Mapping (OIM). Finite element analysis was conducted to investigate and predict the deformation behavior during indentation and correlated very well with the experimental results.

3:30 PM Break

3:40 PM
Microstructure, Wettability and Mechanical Properties of SnZn Solder with Minor Ag Alloying Addition: *Zhidong Xia*[1]; Yongping Lei[1]; Yaowu Shi[1]; Fu Guo[1]; Ran Lu[1]; [1]Beijing University of Technology, The Key Lab. of Advd. Functional Matls., Ministry of Educ. P.R.C, Coll. of Matls. Sci. & Engrg., 100 Ping Le Yuan, Chaoyang Dist., Beijing 100022 China

In view of the cost and availability of raw materials of lead-free solder, tin-zinc solder is still very attractive to microelectronics application. In many electrical and electronic devices, pads on printed circuit board and leads of components are plated with some alloying materials before soldering. In this study, Sn-8Zn, Sn-9Zn, Sn-10Zn alloys with 0.25%Ag additive were investigated considering the wettability of these three solders on electroless tin, silver, nickel plates and pure copper substrate, respectively. Microstructure of the solders obtained during the wetting process was analyzed by optical microscopy and SEM with EDX. Tensile test was conducted to assess the strength and ductility of the solder. SnZn alloy with 0.25%Ag addition showed good wettability on electroless Ag-plated substrate. The effect of zinc variation on the tensile property of the solders was small. The microstructure of Sn-8Zn-0.25Ag and Sn-10Zn-0.25Ag solders was characterized with special shaped intermetallic compound phase, while the microstructure of Sn-9Zn-0.25Ag was basically the SnZn eutectic phase.

4:00 PM
Three-Dimensional Analysis of the Interface Between a Sn-Zn-Bi Solder and a Substrate by Using the Angle-Lapping Method: *Nobuhiro Ishikawa*[1]; [1]National Institute for Materials Science, High Voltage Electron Microscopy Sta., 3-13, Sakura, Tsukuba, Ibaraki 305-0003 Japan

The microstructure of the interface between a Sn-8wt%Zn-3wt%Bi Pb-free solder and a Cu substrate by packaging of ball grid assembly (BGA) process has been studied. For preparing the specimen, angle-lapping method was applied to analyze the interface between solder and substrate three dimensionally by combination with the analysis from cross-sectional direction. Transmission electron microscope (TEM) was used mainly for analysis. The wettability of the solder and the substrate was not bad because there were few voids on both side of the intermetallic compound(IMC) layer formed at the interface. This result is different from the use of Ni-P electroless plate as the substrate. But many cracks were found inside the IMC layer and their distribution was homogeneous. These cracks may affect the mechanical property of the interface. There also found at least five phases stacked inside the IMC layer.

4:20 PM
Controlling Intermetallic Compound Growth in SnAgCu/Ni-P Solder Joints by Nano-Sized Cu6Sn5 Addition: Szu-Tsung Kao[1]; Yung-Chi Lin[1]; *Jenq-Gong Duh*[1]; [1]National Tsing Hua University, Dept. of Matls. Sci. & Engrg., 101 Sec.2 Kuang-Fu Rd., Hsinchu 300 Taiwan

Nanosized Cu_6Sn_5 dispersoids were incorporated into Sn and Ag powders and milled together to form Sn-3Ag-0.5Cu composite solders by mechanical alloying process. In this study, it is aimed to investigate the interfacial reaction between SnAgCu composite solder and electroless Ni-P/Cu UBM after annealing at 240°C for 15 min. The growth of the IMCs formed at composite solder/EN interface was retarded as compared to the commercial Sn3Ag0.5Cu solder joints. With the aid of the elemental distribution by x-ray color mapping in the electron probe microanalysis (EPMA), it is demonstrated that the SnAgCu composite solder exhibited refined structure. It is proposed that the Cu_6Sn_5 additives was pinned on the grain boundary of Sn after annealing and thus retarded the movement of Cu toward the solder/EN interface to form interfacial compounds. In addition, wetting is an essential prerequisite for soldering to ensure good bonding between solder and substrate. It was demonstrated that the contact angles of composite solder paste was less than 25°, indicating good wettability.

4:40 PM
Effect of Electromigration on Intermetallic Compound Growth at the Interfaces Between Ni and Eutectic SnAg(Cu): *Shengquan Ou*[1]; King-Ning Tu[1]; [1]University of California, Dept. of Matls. Sci. & Engrg., 405 Hilgard St., Los Angeles, CA 90095-1595 USA

Formation of intermetallic compound (IMC) at the solder joint interfaces is essential in bonding the parts together. However, excessive IMC formation will cause detrimental effect on the joint strength, e.g., due to Kirkendall void formation. Moreover, under electric current stressing, dramatically different IMC growths at the cathode and anode may become a reliability problem in electronic packaging. We have used eutectic SnAg(Cu) solder lines with Ni wire-electrodes in v-grooves etched on (100) Si surfaces to study the effect of electromigration on IMC growth. The effects of temperature (120 to 180°C), current density (1 to 3E4 A/cm2) and length of the solder line (200 to 800 micron) will be discussed.

5:00 PM
A Study on Tin Whisker Growth on Electroplated Tin in Terms of Substrate, Surface Oxides, and Stress Evolution in Sn-Cu Film: *Dong-Min Jang*[1]; Jin Yu[1]; Taek-Yeong Lee[2]; [1]Korea Advanced Institute of Science and Technology, Matl. Sci. & Engrg., 373-1 Guseong-Dong, Yuseong-gu, Daejon 305-701 S. Korea; [2]Hanbat University, Matl. Sci. & Engrg., San 16-1 Dukmyung-dong, Yuseong-gu, Daejon 305-719 S. Korea

Study of tin whisker growth on pure tin was mostly carried out in 1970's and recently many publications were presented to provide standard acceleration test procedures and growth mechanism. However some disagreement and conflicting results among investigators exist and more systematic understanding is required to resolve tin whiskering. In this study tin whisker growth on electroplated Sn/Cu was investigated. The effect of mechanical polishing of Cu layer before tin plating was presented. Tin whiskers were found only after 12 hours in case of the polished Cu layer. The maximum length of whisker is about 40§- after 3 days. Both compressive stress and surface oxides on tin film are necessary conditions for tin whisker growth, which has not yet been quantitatively measured. The type and amount of surface oxides on tin

film were characterized and stress evolution in Sn/Cu film was measured in-situ at two conditions, air and vacuum at 60C.

5:20 PM
Impact and Thermomechanical Reliability of Sn-Ag-In Solder Joint: *Tatsuya Shoji*[1]; Masayoshi Date[1]; Masaru Fujiyoshi[1]; Koji Sato[2]; [1]Hitachi Metals, Ltd., Metallurgl. Rsch. Lab., 2107-2, Yasugi-cho, Yasugi, Shimane Japan; [2]Hitachi Metals, Ltd., Yasugi Works

Sn-Ag-In ternary alloys were evaluated regarding microstructures and mechanical properties. In the case of Sn-0.3Ag-2In solder bumps, a small number of particles of intermetallic compounds (IMCs) were dispersed within the bulk, and a thin IMC layer was formed at the bond interface with an electroplated Ni/Au pad, compared with Sn-3Ag-0.5Cu solder bumps. Impact reliability of the daisy-chained BGA solder joints was evaluated by using a micro-Charpy impact tester. Impact was applied directly to a substrate whose bond-pads were an electroplated Ni/Au or an organic solder preservative (OSP) coated Cu. The magnitude of the applied impact was changed to investigate its effect on failure lives. We found Sn-Ag-In alloys had longer failure lives than the Sn-3Ag-0.5Cu or the Sn-Pb solder. A thermal cycle test for modules mounted BGA packages was also performed. Sn-Ag-In alloys showed low probability of initial failure compared with that of Sn-3Ag-0.5Cu, although its median life was shorter than that of Sn-3Ag-0.5Cu.

Magnesium Technology 2005: Magnesium and Alloys - Refining, Recycling and Fundamentals

Sponsored by: Light Metals Division, International Magnesium Association, LMD-Magnesium Committee
Program Organizers: Ramaswami Neelameggham, US Magnesium LLC, Salt Lake City, UT 84116 USA; Howard I. Kaplan, US Magnesium LLC, Salt Lake City, UT 84116 USA

Monday PM Room: 2004
February 14, 2005 Location: Moscone West Convention Center

Session Chairs: Ramana G. Reddy, University of Alabama, Tuscaloosa, AL 35487-0202 USA; Ralph Harris, McGill University, Mining, Montreal, Quebec H3A 2B2 Canada

2:00 PM
Castability of Magnesium Alloys: *Amanda L. Bowles*[1]; Qingyou Han[1]; Joe A. Horton[1]; [1]Oak Ridge National Laboratory, Metals & Ceram. Div., 1 Bethel Valley Rd., Oak Ridge, TN 37831 USA

There is intense research effort into the development of high pressure die cast-able creep resistant magnesium alloys. One of the difficulties encountered in magnesium alloy development for creep resistance is that many additions made to improve the creep properties have reportedly resulted in alloys that are difficult to cast. It is therefore important to have an understanding of the effect of alloying elements on the castability. This paper gives a review of the state of the knowledge of the castability of magnesium alloys.

2:20 PM
Microstructure and Phase Transformations in Quasicrystal-Containing Mg-Zn-Y Alloys: *Alok Singh*[1]; Masaki Watanabe[2]; Akira Kato[2]; An-Pang Tsai[3]; [1]National Institute for Materials Science, Matls. Engrg. Lab., 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047 Japan; [2]Toyota Motor Corp., Matls. Engrg. Div. II, Toyota-cho, Toyota, Aichi 471-8572 Japan; [3]Tohoku University, Inst. of Multiplinary Rsch. for Advd. Matls., 2-1-1 Katahira, Sendai, Miyagi 980-8577 Japan

The strength and deformation behavior of quasicrystal-containing dilute Mg-Zn-Y alloys after hot-rolling or extrusion at 400C have recently been reported. These alloys exhibit high ductility with moderate strength and a highly stable microstructure at elevated temperatures. We report here the effect of heat treatment on two extruded alloys Mg95Zn4.2Y0.8 and Mg92.5Zn6.5Y. The quasicrystal particles, facetted and showing a definite orientation relationship with the matrix, become rounded on heating to 400C. In the matrix, fine rods of MgZn2 precursor phase occur parallel to the hexagonal axis. A ternary phase tau1 related to Mg4Zn7 precipitates in the matrix on annealing of alloy Mg95Zn4.2Y0.8, to be replaced by precipitates of quasicrystal phase on further annealing. In the alloy Mg92.5Zn6.5Y, the quasicrystal phase transforms to a hexagonal Mg25Zn58Y17 phase at 400C. The quasicrystal then reprecipitates on its interface, forming a nano-composite. Effects of microstructural changes on the deformation behavior are described.

2:40 PM
Phase Transformation and Creep of Die-Cast Mg-Al-Ca Based Alloys: *Akane Suzuki*[1]; Nicholas D. Saddock[1]; J. Wayne Jones[1]; Tresa M. Pollock[1]; [1]University of Michigan, Matls. Sci. & Engrg., 3062 H.H. Dow, 2300 Hayward St., Ann Arbor, MI 48109 USA

The stability of microstructure and phases in die-cast AC53 and AXJ530 was investigated in detail by TEM. In both alloys, crystal structure of the eutectic intermetallic compound $(Mg, Al)_2Ca$ at grain boundaries was identified as dihexagonal C36 structure. The C36 phase is not stable and transforms into Al_2Ca (C15 structure, cubic) with aging at 573 K. Since this transition proceeds by shearing of the closed-packed planes with crystallographic orientation relationship of $(0001)_{C36}\|\{111\}_{C15}$ and $[2\text{-}1\text{-}10]_{C36}\|[01\text{-}1]_{C15}$, the network structure of intermetallic compound surrounding α-Mg grains is fairly stable after prolonged exposure at elevated temperature. In addition, precipitation of Al_2Ca in α-Mg was observed after 360 ks aging at 573 K. The precipitates have disc-shape with habit plane of $\{111\}_{C15}\|\{0001\}_{\alpha}$. These transformations are caused by ejection of supersaturated Al and Ca from α-Mg phase. Dislocation substructure evolved during creep deformation will be presented, and relationship between creep properties and microstructure will be discussed.

3:00 PM
Grain Refinement of Mg Alloys by Nanoscaled TiN Particles: *Gabriele Vidrich*[1]; Oliver Moll[1]; Hans Ferkel[1]; [1]TU Clausthal, Inst. for Matls. Sci. & Tech., Agricolastr. 6, Clausthal-Zellerfeld 38678 Germany

A new method was developed which allows a grain refinement of Mg alloys via casting from Mg melts containing nanoscaled TiN particles. The dispersed particles in the melt act as nucleation sites of Mg grains during solidification. Grain refinement was observed by light-microscopy of ingots which were cast from AZ91 melts containing dispersed TiN nanoparticles of particle volume fraction in the melt below 0.2 %. Structure investigations were also carried out by electron microscopy and X-ray diffraction. It was shown that TiN nanoparticles are stable in AZ91 melt for several hours at 700°C. This is a requirement to gain a heterogeneous nucleation of Mg grains on TiN seeds. The results are discussed.

3:20 PM
Inspection of Grain Boundary Sliding in Die-Cast Mg Alloys During Creep Deformation Via Strain Mapping Techniques: *Nicholas David Saddock*[1]; Tresa M. Pollock[1]; Akane Suzuki[1]; Samuel Charles Wildy[2]; J. Wayne Jones[1]; [1]University of Michigan, Matl. Sci. & Engrg., 2300 Hayward Rd., 3062 H.H. Dow, Ann Arbor, MI 48109 USA; [2]University of Oxford, Dept. of Matls., Parks Rd., Oxford OX 13Ph UK

Numerous aluminum containing, magnesium-based die-cast alloys (e.g. AZ91, AS21, AE42 and AC53) exhibit a transition from power law creep at intermediate stresses to a stress dependence of 1-2 at low stresses, indicating the possibility of change in creep mechanism from grain boundary sliding (GBS) to dislocation controlled processes. However, direct experimental evidence of GBS is seldom reported, especially at lower strains. In the present study a high-resolution strain mapping technique developed in previous studies is employed to examine the accumulation of strain during creep of AM50 and AXJ530, the latter containing 3 wt. % calcium. The influence of Ca on the morphology and stability of grain boundary microstructure and its corresponding influence on the development of strain localization in these alloys is explored. Microstructural evolution and the development of dislocation structure, as ascertained by TEM will be described, along with the mechanisms for creep deformation in these alloys at low stresses.

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The Development of New Additions for Liquid Magnesium: Kang Sun[1]; *Stavros A. Argyropoulos*[1]; Tim Kosto[2]; [1]University of Toronto, Matls. Sci. & Engrg., 184 College St., Toronto, Ontario M5S3E4 Canada; [2]Milward Alloys, Lockport, NY 14094-1712 USA

The exothermic behavior of the intermetallic reactions inside various metallic powder compact and its assimilation fundamentals in molten magnesium were examined. The work was focused on two types of compacts. Specifically Mn-Al and V-Al compacts were examined. In this research work cylindrical compacts were manufactured and tested. The experimental work involved simultaneous temperature measurements of three thermocouples as well as detection of the apparent weight of the cylindrical specimen during its assimilation in liquid magnesium. The details of the intermetallic reactions prior to the compact complete disintegration were investigated by microscopically studying the morphology and local composition in a partially

reacted compact. The exothermic reaction increases the compact's temperature above that of the liquid magnesium. In tandem with this exothermic reaction, the compact is suffering a swelling action. This swelling action disintegrates the cylindrical specimen, which is assimilated into the liquid magnesium.

4:15 PM
Numerical Simulations of Radiative Heat Transfer Between High-Temperature Fluidized Beds and Magnesium Castings: *Saytavur Ispandiyar Bakhtiyarov*[1]; [1]Auburn University, Mech. Engrg., 202 Ross Hall, Auburn, AL 36849-5341 USA

Fluidized beds are considered as an efficient alternative to conventional heat treatment operations. The advantages of fluidized beds heat treatment processes are (1) a very high heat treatment rates, (2) temperature uniformity, flexibility of the fluidized bed furnaces (they can operate at any temperature and with any atmosphere, (4) the process is simple to operate and untrained persons can operate furnace and set process parameters. However, the radiative heat transfer in fluidized bed furnaces was not studied systematically in the literature. Existing theoretical models for predicting radiative heat transfer between fluidized beds and castings usually use the Stefan-Boltzman equation. These models require the total effective radiative coefficient to be obtained experimentally. This paper presents the results of numerical simulations, where the absorption coefficient is defined as a function of bed characteristics.

4:35 PM
Scale-Up of Magnesium New Rheocasting from a Laboratory Level to an Industrial Process: *Werner Fragner*[1]; Matthias Gruber[2]; Gernot Macher[2]; [1]ARC Light Metals Competence Center Ranshofen GmbH, Casting Tech., Postfach 26, Ranshofen, Upper Austria 5282 Austria; [2]Non Ferrum Metallpulver Ges.m.b.H. & Co. KG, Austria, PO Box 11, St. Georgen bei Salzburg, Salzburg 5113 Austria

Sludge, dross and black dross are among the most demanding by-products of Magnesium handling and recycling. They are reactive when coming into contact with water including hydrogen and ammonia formation. Especially black dross is a recycling problem being very reactive with its fine magnesium particles and high salt and magnesium oxide content. Together with LKR Non-Ferrum developed a way of treating these by-products either in a dry or a wet way, depending on the incoming material and recovering its components that are magnesium, magnesium oxide and salt. The products from both processes can be reused and are not reactive. With the recovery of metallic Mg the treatment is an economical and ecological feasible way to process sludge, dross and black dross.

4:55 PM
Economic Analysis of the Carbothermal Production of Magnesium: *Robert R. Odle*[1]; Andrew W. McClaine[2]; Jens Frederiksen[3]; [1]Metallurgical Viability, Inc., 60 Blue Hen Dr., Ste. 3000, Newark, DE 19713 USA; [2]Safe Hydrogen, LLC, 30 York St., Lexington, MA 02420-2009 USA; [3]PF&U Mineral Development ApS, Kullinggade 31 5700 Svendborg DK

A techno-economic model of a novel carbothermal process for the production of magnesium using Magnesium Technologies Limited (MTL) patented process has been carried out. Feedstock for the process is a relatively pure MgO recycled from Safe Hydrogen's Magnesium Hydride Slurry Process for hydrogen production, transportation, and storage. The model allows the user to alter design assumptions on most unit operations, composition and cost of selected raw materials, some project conditions including metal prices, labor costs, staffing, and energy costs. The model demonstrates the power of Visual Basic for Applications (VBA) coupled with an Excel Spreadsheet interface for producing steady state material and energy balances, income statements, and an estimate of gross profits for the conditions selected. The model facilitates "what-if" analysis and allows the user to intuitively establish the critical assumptions/conditions for economic viability. The carbothermal process for magnesium promises a relatively simple, automated process with low capital costs and competitive operating costs compared to electrolytic and silicothermic processes. The application of this technology has been limited by the lack of a method to rapidly cool the Mg(vapor) and CO to prevent the back reaction. MTL is developing a technology that promises to solve this problem. Safe Hydrogen is interested in evaluating this technology since their hydrogen storage technology used with a fuel cell technology becomes competitive with gasoline powered internal combustion engines as the price of magnesium drops.

5:15 PM
Co-Existing Phases in the Al-Ca-Mg System: Rai Raz[1]; Shaul Avraham[1]; *Menahem Bamberger*[1]; [1]Technion, Dept. of Matls, Engrg., Technion City, Haifa 32000 Israel

The use of Mg alloys at elevated temperature application can contribute to weight reduction both in critical components and overall weight, that will lead to economical and environmental benefits. The elevated temperature mechanical properties of Mg-Al-Ca alloys is comparable to those of RE alloys. This behavior is attributed to the formation of Al_2Ca precipitates and the fine microstructure of these alloys. The Al-Ca-Mg system is yet to be thoroughly studied. This work will present recent results related to the ternary Al-Ca-Mg phase diagram, which are essential for further thermodynamical simulations.

Magnesium Technology 2005: Wrought Magnesium Alloys II

Sponsored by: Light Metals Division, International Magnesium Association, LMD-Magnesium Committee
Program Organizers: Ramaswami Neelameggham, US Magnesium LLC, Salt Lake City, UT 84116 USA; Howard I. Kaplan, US Magnesium LLC, Salt Lake City, UT 84116 USA

Monday PM — Room: 2006
February 14, 2005 — Location: Moscone West Convention Center

Session Chairs: Sean R. Agnew, University of Virginia, Dept. of Matl. Sci. & Engrg., Charlottesville, VA 22904-4745 USA; Peter Pinfold, Fluor Corp, Alcoa, TN 37701 USA

2:00 PM
Microstructural Evolution During Severe Deformation of AZ-31 Magnesium Alloy Under Non-Isothermal Process Condition: *Yi Liu*[1]; *Amit K. Ghosh*[1]; [1]University of Michigan, Matls. Sci. & Engrg., 2300 Hayward St., Ann Arbor, MI 48109 USA

Large plastic deformation was imparted to Mg alloy plate AZ-31B by compressing along the in-plane direction, in progressive stages below 300C, via non-isothermal processing method and under superimposed hydrostatic pressure. It was shown that by progressively lowering the deformation temperature, microstructures of ultrafine grain size, approaching nanocrystalline structure could be obtained. Starting from a bimodal grain structure, the volume fraction of fine grains increased significantly as grain subdivision by twinning mechanism was utilized to achieve grain refinement. X-ray diffraction results indicated that a strong basal fiber texture emerged normal to the original plate rolling direction, as a result of the new deformation mode, and a very high strength level for such alloys resulted due to reduced dynamic recovery effects.

2:20 PM
Bendability and Microstructure of Magnesium Alloy Tubes at Room and Elevated Temperatures: *Alan A. Luo*[1]; Anil K. Sachdev[1]; Raja K. Mishra[1]; [1]General Motors Research & Development Center, Matls. & Processes Lab., 30500 Mound Rd., MC 480-106-212, Warren, MI 48090 USA

This paper investigates the bendability and microstructure of magnesium alloy AZ31 tubes at room and elevated temperatures. The results suggest limited bendability for magnesium alloy tubes at room temperature. Microstructural analysis indicates that strain localization caused by twinning initiates cracks at the surface which consequently lead to fracture upon room-temperature bending. A moderate temperature (150-200°C) bending process has been developed for magnesium alloy tubes. Microstructural evaluation indicates that twinning is an important deformation mechanism in moderate temperature bending. A significant amount of localized dynamic recrystallization is evident at prior grain boundaries when bending at above 200°C.

2:40 PM
An Internal Variable Approach to the Superplastic Deformation of AZ31 Magnesium Alloy: *Hyunseok Lee*[1]; Won Kyu Bang[2]; Hwan Jin Sung[2]; Young Won Chang[1]; [1]Pohang University of Science & Technology, Matl. Sci. & Engrg., San 31, Hyoja-dong, Nam-gu, Pohang, Kyung-buk 790-784 S. Korea; [2]Research Institute of Industrial Science & Technology, San 32, Hyoja-dong, Nam-gu, Pohang, Kyung-buk 790-600 S. Korea

Internal variable theory, proposed by Chang et al., has manifested as an inelastic deformation model based on the dislocation dynamics. The constitutive model is formulated with internal variables corresponding to the deformation state of the material, accordingly has more solid physical basis. In the previous studies, the theory can be demonstrated as a useful method for the interpretation of the structural superplasticity and has been applied successfully for various metallic materials. In the present study, a series of tensile tests of AZ31

magnesium alloy has been carried out to investigate superplastic deformation behavior with temperature variation. Analysis of load relaxation test results based on internal variable theory gave further information about superplastic deformation and its accommodation mechanism.

3:00 PM
Infrared Processing and Hot Rolling of Magnesium Alloys: *Joe A. Horton*[1]; Amanda L. Bowles[1]; Craig A. Blue[2]; Sean R. Agnew[3]; [1]Oak Ridge National Laboratory, Metals & Ceram. Div., Bldg. 4500S-MS6115, PO Box 2008, Oak Ridge, TN 37830 USA; [2]Oak Ridge National Laboratory, Metals & Ceram. Div., Bldg 4508-MS6083, PO Box 2008, Oak Ridge, TN 37831-6083 USA; [3]University of Virginia, Matls. Sci. & Engrg., 116 Engr.'s Way, Charlottesville, VA 22904-4745 USA

It is of interest to produce magnesium wrought products more efficiently in order to make them more attractive for applications. Use of radiant heating by infrared or plasma arc lamps have the potential to reduce processing steps and thereby save time and cost. Previous studies at a commercial rolling facility equipped with infrared lamps have shown that this process is feasible with AZ31B. Comparisons of microstructures, mechanical properties, and crystallographic textures for various hot rolling temperatures attained by pack rolling will be presented and correlated with the infrared processing results. Research sponsored by the U.S. Department of Energy, Assistant Secretary for Energy Efficiency and Renewable Energy, Office of FreedomCAR and Vehicle Technologies, as part of the High Strength Weight Reduction Materials Program, under contract DE-AC05-00OR22725 with UT-Battelle, LLC.

3:20 PM
The Types and Roles of Deformation Twinning in AZ31 Mg Alloys: *Junichi Koike*[1]; Takeo Miyamura[1]; Akira Nishinoiri[2]; Manabu Enoki[2]; [1]Tohoku University, Dept. of Matls. Sci., 02 Aoba, Aramaki, Aoba-ku, Sendai 980-8579 Japan; [2]University of Tokyo, Dept. of Matls. Sci., Hongo, Bunkyo-ku, Tokyo Japan

Rolled sheets of AZ31 magnesium alloys were tensile tested at room temperature. Twinning behavior was observed at various strain levels up to a pint of fracture, using an optical microscope, an orientation imaging microscope and an acoustic emission system. Twinned area was increased in two separate stages with strain. Initial rapid increase was observed near the yield point, due to the formation of wide lenticular twins. This was followed by another rapid increase close to the failure point, due to the formation of narrow banded twins. Acoustic emission (AE) signals also exhibited two separate stages with strain, which enabled us to relate each twin type with FFTed AE signals. The each type of twin will be discussed in light of its role on deformation and fracture mechanisms.

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Adapted Extrusion Technology for Magnesium Alloys: *Jan-F. Lass*[1]; Friedrich-W. Bach[1]; Mirko Schaper[1]; [1]University of Hannover, Inst. of Matls. Sci., Schönebecker Allee 2, Hannover D-30823 Germany

The rising efforts for an ecologically harmless capacity increase of technical products and processes not only in the automobile industry result in the renaissance of magnesium within the last years. Therefore a variety of magnesium components are already applied in automobiles. But this is nearly restricted to diecasting components. One reason for this is the extremely limited spectrum of adequate magnesium wrought alloys and above all the extrusion technology for the production of adequate profiles which is not explored very well. Especially in the construction of automobiles, increased attempts are made to apply magnesium in bearing structures. Therefore it is necessary to develop an adequate and economical materials processing for the extrusion of magnesium alloys. Moreover also a process method must exist which specifically influences the material properties of extruded magnesium profiles. This article gives a general view about the problems and difficulties which are included in the extrusion process as well as in the resulting material properties of extruded magnesium profiles. Furthermore several possibilities will be described to solve these problems in different ways. Here the examination of the initial materials and their properties, the whole extrusion process as well as the subsequent treatment of the extruded magnesium profiles is very important.

4:15 PM
Constitutive Behavior of AZ31B Mg Sheet: Development and Implementation of Constitutive Model: *Min Li*[1]; XiaoYuan Lou[1]; Frederic Barlat[2]; Robert H. Wagoner[1]; [1]Ohio State University, Dept. of Matls. Sci. & Engrg., 2041 College Rd., 477 Watts Hall, Columbus, OH 43210 USA; [2]Alcoa Inc., Alcoa Techl. Ctr., Matls. Sci. Div., 100 Techl. Dr., Alcoa Ctr., PA 15069 USA

The mechanical response of basal-textured AZ31B magnesium sheet has been measured in uniaxial tension, in-plane compression, and simple shear using recently developed tests. Reversed paths have been imposed using the same tests. Twinning occurs in compression and untwinning occurs in subsequent tension, with consequently lowered yield stress and rapid work hardening. The yielding asymmetry and unusual evolution and reversal of hardness are difficult to model with standard plasticity formulations. A new formulation has been developed to reproduce the key features of the path dependence of hardening with a view toward implementation in commercial finite element programs. Using such a capability, it may be possible to devise novel forming techniques to take advantage of the unusual room-temperature behavior of AZ31B.

4:35 PM
Microstructure Development of Extruded Mg Alloys: *Soeren Mueller*[1]; Klaus Mueller[2]; Walter Reimers[1]; [1]Technical University, Inst. for Matls. Sci. & Tech., Ernst-Reuter-Platz 1, Sekr. BH 18, Berlin 10587 Germany; [2]Technical University, Extrusion R&D Ctr., Gustav-Meyer-Allee 25, Sekr. TIB 4/1-2, Berlin 13355 Germany

In order to obtain light-weight constructions in the automobile and aircraft industry the extrusion of magnesium profiles is an important factor. Magnesium profiles of the AZ alloy family have been extruded in the direct, indirect and hydrostatic extrusion method at the extrusion research and development center of the Technical Universtity of Berlin. These profiles were then tested at the institute for materials science and technology of the Technical Universtity of Berlin for their microstructure. Thereby the different samples exhibited a different microstructure as well as different mechanical properties. Some of these samples were taken to another deformation after the extrusion process and then also tested for their microstructure and mechanical properties. The following paper will discuss the difference in the extrudates coming from the direct, indirect and hydrostatic extrusion as well as the extrudates which were further deformed in order to optimize the mechanical properties.

4:55 PM
Constitutive Behavior of AZ31B Mg Sheet: Measurement and Analysis of Mechanical Properties: *Xiaoyuan Lou*[1]; Richard K. Boger[1]; Frederic Barlat[2]; Robert H. Wagoner[1]; [1]Ohio State University, Dept. of Matls. Sci. & Engrg., 477 Watts Hall, 2041 College Rd., Columbus, OH 43210 USA; [2]Alcoa Technical Center, Matls. Sci. Div., 100 Techl. Dr., Alcoa Ctr., PA 15069 USA

HCP alloys have a limited number of non-basal slip systems available. For basal-textured AZ31B magnesium sheet, the activation energy for twinning is asymmetric, leading to a strong difference in the tensile and compressive flow curves. To provide information on the competition of deformation mechanisms of slip, twinning, and untwinning, the mechanical behavior of AZ31B was examined under non-proportional load paths. Techniques have been developed to deform magnesium sheet under in-plane tension/compression and reversed, simple shear. Acoustic emission techniques were used in conjunction with the mechanical tests to detect and quantify the twinning and untwinning mechanism. The results of the mechanical testing are used in combination with the initial and deformed texture to inform the development of a new constitutive model for this alloy.

5:15 PM
In-Situ Investigation of Twinning Behaviour in Mg-3Al-1Zn: *Zohreh Keshavarz*[1]; Matthew R. Barnett[1]; [1]Deakin University, Sch. of Engrg. & Tech., Pigdons Rd., Geelong, VIC 3217 Australia

Magnesium alloys are attractive for automotive and aerospace industries, due to their low density. One problem with these alloys is their limited formability at room temperature. Twinning plays a dominant role in deformation behaviour and it can be expected that an increased understanding of twinning will help improve formability. In the present work, the behaviour of different twinning systems in as-cast Mg-3Al-1Zn is investigated using in-situ tensile tests in a scanning electron microscope. Electron backscatter diffraction and back scatter electron imaging were carried out during the tests. The results show both tension and compression twinning are active at room temperature and that twinning and untwinning occur both during loading and unloading.

Materials Processing Fundamentals: Liquid Metal Processing

Sponsored by: Extraction & Processing Division, Materials Processing & Manufacturing Division, EPD-Process Fundamentals Committee, MPMD/EPD-Process Modeling Analysis & Control Committee

Program Organizers: Princewill N. Anyalebechi, Grand Valley State University, Padnos School of Engineering, Grand Rapids, MI 49504-6495 USA; Adam C. Powell, Massachusetts Institute of Technology, Department of Materials Science and Engineering, Cambridge, MA 02139-4307 USA

Monday PM Room: 3001
February 14, 2005 Location: Moscone West Convention Center

Session Chair: Prince N. Anyalebechi, Grand Valley State University, Padnos Sch. of Engrg., Grand Rapids, MI 49504-6495 USA

2:00 PM
Flow Conditions at the Meniscus of a Continuous Casting Mold Through a Physical Model Approach: Carlos Antonio Silva[1]; *Varadajan Seshadri*[2]; Itavahn Alves Silva[1]; Versiane Albis Leão[1]; Dimas Bahiense Moreira[3]; [1]Universidade Federal de Ouro Preto, Escola de Minas/Engrg. Metalúrgica, Campus do Morro do Cruzeiro S/N, Ouro Preto, Minas Gerais 35400-000 Brazil; [2]Universidade Federal de Minas Gerais, Metallurgl. Engrg., Rua Espirito Santo, 35, Belo Horizonte, Minas Gerais Brazil; [3]Cia Siderurgica Tubarao, Av. Brigadeiro Eduardo Gomes 930, Serra, Espirito Santo 29163-970 Brazil

Internal and sub-superficial defects of continuously cast steel plates have been associated with flow conditions at the metal-slag interface. Turbulence plays a main role in regard to emulsification of top slag and entrapment of inclusions. The objective of this study was to evaluate the flow pattern as a function of SEN geometry and operating conditions. A 1:1 physical model was used in order to allow testing of actual nozzles. A custom made sensor was developed for measuring sub-surface velocity midway. Experimental data as well as flow visualization indicate a high degree of superficial turbulence for some combinations of geometry and nozzle penetration. These combinations are indicated as detrimental to steel quality.

2:25 PM
Thermodynamics on the Solidificational Refining of Si with Si-Al Melts: *Takeshi Yoshikawa*[1]; Kazuki Morita[1]; [1]University of Tokyo, Dept. of Matls. Engrg., 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656 Japan

Recently, the amount of solar cell production, especially that of polycrystalline silicon, increases significantly with a growing demand for clean energy. Solar grade silicon (SOG-Si), however, would be short of supply with increasing demand because of its dependence on a semiconductor industry. Therefore the development of an innovative low-cost mass production system for polycrystalline silicon is required. The authors have been trying to develop the low temperature silicon refining process, "solidification refining of silicon with Si-Al melts at 1173-1273K". In this study, segregation ratios of impurities such as B, P, Fe, etc., between solid Si and Si-Al melt were experimentally or theoretically determined to evaluate the potency for purification in this process. For almost all impurities, segregation ratio at 1273K was obtained much smaller than segregation coefficient between solid/liquid Si, therefore low temperature solidification process is found to be more effective for purification compared with ordinal solidification refining.

2:50 PM
Measurement of Natural Convection in Ga Melts With and Without Applied Magnetic Fields: *B. Xu*[1]; *Ben Q. Li*[1]; [1]Washington State University, Sch. of Mechl. & Matls. Engrg., Pullman, WA 99164 USA

Results from an experimental study on natural convection induced by temperature gradient in molten gallium contained inside a rectangular container are presented. The damping effect of the convective flow from an externally applied static magnetic field is investigated. Induced velocity and temperature fields are mapped using a standard constant temperature hot-film anemometry and a thermocouple with and without the applied magnetic field, respectively. Detailed experimental setup and procedure are depicted in the present paper. Obtained velocity and temperature profiles are examined against previous numerical simulations and reasonably good agreement has been achieved. Obvious damping effect can be observed in both the temperature and the velocity profiles when the external magnetic field presents.

3:15 PM
Numerical Simulation of Molten Steel Flow Under FC Mold Magnetic Field: *Hwasoo Park*[1]; Misun Im[1]; [1]Kookmin University, Advd. Matls. Engrg., Jung-Nung 3Dong,Sung-Buk Ku, Seoul 136-702 Korea

Numerical simulation has been performed to analyze the characteristics of a molten steel flow in the continuous casting process. Momentum and energy equation has been coupled considering the solidification of steel along with turbulence ê-å model. The vertical bending mold has bifurcated nozzle with 15 degrees of downward angle and FC mold supplies DC induced magnetic fields. The discrete phase model is employed to calculate the molten metal-argon gas flow with Rosin-Rammler distribution law and cloud particle tracking method. Magnetic fields not only change the magnitude of flow vectors but also the direction of flow especially near corner area . They suppress the velocity vectors at port outlet and increase the steel temperature at free surface and inside the mold.

3:40 PM Break

3:55 PM
Evaluation of Y2O3 as Front Layer of Ceramic Crucibles for Vacuum Induction Melting of TiAl Based Alloys: *Jose Joaquim Barbosa*[1]; Carlos Silva Ribeiro[2]; Antonio Caetano Monteiro[1]; [1]University of Minho, Mechl. Engrg., Campus de Azurem, Guimaraes 4800-058 Portugal; [2]University of Porto, FEUP, Rua Roberto Frias, Porto 4200-465 Portugal

During the last decades titanium alloys were found to be valuable engineering materials for many different applications. Formerly used in critical applications like aerospace, aeronautic and military equipment, where the factor cost is not relevant, titanium alloys are finding now new and different markets. However, the development of such new markets will depend on an effective cost reduction of titanium parts, in order to achieve a selling cost suitable with its application in consumer goods. A possible solution to decrease production costs might be the use of traditional casting techniques to produce near net shape functional parts. During the last years, the authors have developed extensive research work on this field, and a new technique both for melting and moulding, using ceramic multi-layered crucibles and investment casting shells was developed. This paper presents some of the results obtained during that research work: a Ti-48Al alloy was melted and cooled inside CaO, MgO and Y2O3 stabilized ZrO2 crucibles with inside layer of Y2O3. The chemical composition, hardness and microstructure at the metal-crucible interface, studied by secondary ion mass spectrometry, SEM/EDS and XRS are presented. On a second step, the same alloy was melted on the same crucibles, and poured into graphite moulds, and the crucibles wall was characterized by SEM/EDS and XRS.

4:20 PM
Simulation of Decarburization of a High Alloyed Liquid Steel Using the Reactor Module of Thermo-Calc: *Lina Kjellqvist*[1]; Bo Sundman[1]; [1]Royal Institute of Technology, Dept. of Matl. Sci. & Engrg., SE-10044, Stockholm Sweden

Thermodynamic software and databases are now powerful and accurate enough to give reliable results when applied to complex processes like the decarburization of liquid steels. The reactor module in Thermo-Calc makes it possible to simulate the reduction of carbon in a liquid high alloyed steel by a mixture with oxygen and argon gases. The process is divided into a small number of local equilibria and the gas, liquid and slag phases are distributed between them based on experimental results and fluid flow simulations. A test case using a stainless steel will be compared to experimental data demonstrating the powerful user interface. Future work will lead to an integration of the thermodynamic software in the fluid flow simulations and the additions of S and P in the thermodynamic simulations.

4:45 PM
Modeling of Scrap Melting in an EAF: Diancai Guo[1]; *Gordon A. Irons*[1]; [1]McMaster University, Steel Rsch. Ctr., 1280 Main St. W., Hamilton, Ontario L8S 4L7 Canada

Scrap melting in an EAF is modeled numerically to gain some insight into the heat utilization during a heat. Scrap movement, gas flow and heat exchange are simulated, heat loss and burner heating efficiency discussed. The model enables to determine how much heat the charge can gain from burners before it is melted, the temperature distribution of the scrap pile during melting process, and how much heat lost through radiation and convection to furnace wall and roof.

5:10 PM
Preliminary Investigation of Fluid Mixing Characteristics in Bath During Side and Top Combined Blowing AOD Refining Process of Stainless Steel: *Ji He Wei*[1]; Hong Li Zhu[1]; Guo Min Shi[2]; Qing Yan Jiang[2]; Sen Long Yang[1]; Xin Chao Wang[1]; Jin Chang Ma[1]; He Bing Chi[2]; Li Bing Che[2]; Kai Zhang[2]; [1]Shanghai University, Dept. of Metallic Matls., 149 Yan Chang Rd., Shanghai 200072 China; [2]The Shanghai No. 1 Iron and Steel Company Ltd, Bao Steel (Group) Corporation, W. Changjiang Rd., Shanghai China

The mixing characteristics of the fluid in the bath of 120 t AOD converter during the refining process of stainless steel with side and top combined blowing have been preliminarily examined on a water model unit. The geometric similarity ratio between the model and its prototype (including the side tuyeres and the top lance) was 1:4. Based on the theoretical calculations for the parameters of the gas stream in the tuyeres and the lance, the gas blowing rates used for the model have been more reasonably determined. The influence of the tuyere number and position, and the gas flow rates for side and top blowing on the mixing characteristics has been considered. The results demonstrated that the fluid in the bath underwent vigorous circulatory motion during the blowing, without obvious dead zone in the bath, resulting a well mixing effectiveness. the gas flow rate of the main-tuyere had a governing role on the characteristics, and the gas jet of sub-tuyere can increase mixing efficiency, and the gas jet from the top lance can prolong the mixing time. Corresponding to the specified oxygen top blowing flow rate by the technology, six side tuyeres with an angle of 27 degree between each tuyere, five side tuyeres with an angle of 22.5 or 27 degree can all reach an essentially equivalent and good mixing effectiveness. The relationships of the mixing time with the gas blowing rates of the main-tuyeres and sub-tuyeres and top lance, the angle between each tuyere, and the tuyere number have been obtained.

Mechanical Behavior of Thin Films and Small Structures: Plasticity and Deformation Mechanisms at Small Length Scale

Sponsored by: Structural Materials Division, SMD-Mechanical Behavior of Materials-(Jt. ASM-MSCTS), MPMD-Nanomechanical Materials Behavior

Program Organizers: Xinghang Zhang, Texas A&M University, Department of Mechanical Engineering, College Station, TX 77843-3123 USA; Brad L. Boyce, Sandia National Laboratories, Materials and Processes Sciences Center, Albuquerque, NM 87185 USA; Evan Ma, Johns Hopkins University, Department of Materials Science & Engineering, Baltimore, MD 21218 USA; Andrew Minor, Lawrence Berkeley National Laboratory, National Center for Electron Microscopy, Berkeley, CA 94720 USA; Christopher L. Muhlstein, Pennsylvania State University, Department of Materials Science & Engineering, University Park, PA 16802 USA; Judy A. Schneider, Mississippi State University, Department of Mechanical Engineering, Mississippi State, MS 39762 USA

Monday PM — Room: 2024
February 14, 2005 — Location: Moscone West Convention Center

Session Chairs: Evan Ma, Johns Hopkins University, Dept. of Matls. Sci. & Engrg., Baltimore, MD 21218 USA; David J. Srolovitz, Princeton University, Dept. of Mechl. & Aeros. Engrg., Princeton, NJ 08544 USA

2:00 PM Invited
Deformation at the Nanometer and Micrometer Length Scales: Effects of Strain Gradients and Dislocation Starvation: *William D. Nix*[1]; Gang Feng[1]; Julia R. Greer[1]; [1]Stanford University, Dept. Matls. Sci. & Engrg., 416 Escondido Mall, Stanford, CA 94305-2205 USA

Size effects in plasticity are now well known. Plastic deformation in small volumes requires higher stresses than are needed for plastic flow of bulk materials. Here we review the various effects that appear to be responsible for this. The size dependence of the hardness of metals at the micron scale can be described in terms of the geometrically necessary dislocations or, correspondingly, the strain gradients, created in small indentations. But such accounts break down when the size of the deformation volume begins to approach the spacing of individual dislocations or when the crystal becomes dislocation starved. Nanoindentation of epitaxial films at the nanometer depth scale reveals irregular load-displacement curves. In this domain the nucleation of dislocations and plasticity under dislocation-starved conditions appears to be more important than strain gradients. Recent uniaxial compression experiments on tiny samples of gold made by focused ion beam machining and integrated circuit fabrication methods show strong size effects on plasticity, with sub-micron sized crystals showing remarkable strengths after plastic deformation. These experiments involve small deformation volumes and minimal strain gradients. These size effects may be explained by considering a process of strain hardening by dislocation starvation, wherein existing dislocations leave the crystal more frequently than they reproduce themselves by multiplication.

2:25 PM
Contact-Induced Plasticity of Rough Surfaces Under Nanoindentation: E. Buchovecky[1]; *F. Sansoz*[1]; [1]University of Vermont, Mechl. Engrg., 33 Colchester Ave., 201 Votey Bldg., Burlington, VT 05405 USA

The contact mechanics between two nanoscale surfaces has drawn considerable interest in recent years because of its importance to MEMS tribology, nanoindentation, scanning probe microscopy, and coating deformation. Despite current knowledge that nanostructured film surfaces are not perfectly flat at the nanoscale, the influence of surface asperities on contact mechanics during nanoindentation is not fully understood. In addition, it is unclear how the presence of surface asperities, which create highly-stressed points of contact, significantly alters the incipient plasticity of indented films. In this study, we measure and analyze though atomic force microscopy the topography of nanocrystalline Ni surfaces of different grain size. The quasicontinuum method is then used to model the nanoindentation of rough Ni surfaces. The response of atomically-flat, stepped, and experimentally observed surface profiles is modeled under either cylindrical or prismatic indenter geometries. This study demonstrates the key role of surface roughness on the onset of plasticity in indented films and coatings.

2:40 PM
Critical Shear Stress for Onset of Plasticity in Nanocrystalline Cu Films Determined by Using Nanoindentation: *Ji Chen*[1]; Wei Wang[1]; Ke Lu[1]; [1]Institute of Metal Research, Shenyang Natl. Lab. for Matls. Scis., Shenyang 110016 China

Molecular-dynamics simulations have indicated that with the reduction of grain size, the plastic deformation in nc materials gradually changed from a mixture of intergranular and intragranular processes to GB activities dominated mechanisms.[1,2] However, experimental results to verify this argument are still scarce. The critical shear stress (τ_c), which is directly related to the microscopic deformation mechanisms, can be measured by means of nanoindentation.[3] The present work is to investigate the relationship of τ_c with grain sizes of nc Cu ranging from 5 nm to 60 nm. For all nc Cu films, an obvious deviation from the theoretically elastic reponse was detected at approximately the same critical load and depth about 0.0037 mN and 2.7 nm, respectively, which is much smaller compared with that of single crystal Cu. The measured τ_c for the nc Cu was about 7.3 GPa, which is four magnitudes of orders larger than Peierls-Nabarro barrier for the movement of preexsiting lattice dislocations, and very close to the theoretical shear strength for Cu. The high τ_c of the nc-Cu samples may originate from the suppressed lattice dislocation activities by the ultrafine crystallites, and at the same time, the inactive GB accommodation mechanisms at room temperature under the quasi-static indentation. [1]Van Swygenhoven H, Spaczer M, Caro A. Acta Mater 1999;47:3117. [2]Van Swygenhoven H. Science 2002;296:66. [3]Chen J, Wang W, Qian LH, Lu K. Scripta Mater 2003;49:645.

2:55 PM
Simulations of Nanoindentation in Thin Amorphous Metal Films: Yunfeng Shi[1]; *Michael L. Falk*[1]; [1]University of Michigan, Matls. Sci. & Engrg., 2300 Hayward St., Ann Arbor, MI 48109-2136 USA

A series of molecular dynamics simulations of nanoindentation in a two-dimensional model of a thin metallic glass film exhibit varying degrees of shear localization below the indenter depending on the means of glass processing. The indenter is circular, and all tests were performed at 9.2% of the glass transition temperature (Tg). The glasses were created from a melt 7.7% above Tg by: (I) quenching gradually over a period of approximately 0.5 μs, (II) quenching quickly over a period of approximately 10 ns, and (III) quenching instantaneously from a well-equilibrated liquid state. Indentation was performed at approximately 0.3 m/s to a depth of 8nm. During nanoindentation shear bands nucleated at an indentation depth of approximately 15 Å in the gradually quenched samples. In the shear band region material that previously exhibited local quasi-crystal-like structural ordering transformed into purely amorphous material under deformation. This structural transition appears to be related to the softening mechanism that results in strain localization in the material. Substantially less

localization occurred in samples produced by higher rates of quenching.

3:10 PM Invited
Evolution of Asperity Contacts: *David J. Srolovitz*[1]; Pil-Ryung Cha[1]; Ji-Hee Kim[1]; Jun Song[1]; [1]Princeton University, Dept. of Mechl. & Aeros. Engrg., Princeton, NJ 08544 USA

Contacts between opposing surfaces are key aspects of many MEMS switching devices. At low forces, contact is incomplete and is dominated by bumps or asperities on the surface. In this presentation we examine the evolution of asperities under mechanical, capillarity and electromigration driving forces. In the first study, we perform a series of molecular dynamics studies of single asperity contact under constant displacement rate conditions. The dislocation nucleation, migration and annihilation mechanisms are determined in loading and unloading and correlated with the measured force-displacement curve and the change in the contact area. From this, we determine how contact resistance evolves. The force-displacement behavior and the evolution of the contact resistance are shown to be in excellent agreement with cantilever-based experiments. In the second study, we employ phase field methods to examine the evolution of an asperity contact via surface diffusion, driven by capillarity and electromigration. At zero applied field, surface tension quickly rounds the sharp corners at the contact. If the contact is initially narrow, capillarity can lead to the breaking of the contact, but if it is wide, capillarity broadens the contact. With increasing electric field, surface tension still dominates at short times, followed by the electromigration induced broadening of the contact. Based upon the morphology evolution results, we monitor the concommitant change in the contact resistance. Implications for the evolution of contact resistance in devices will be discussed.

3:35 PM Break

3:50 PM
On the Mechanism of Creep-Controlled Electromigration-Induced Drift: *Joris Proost*[1]; Jan D'Haen[2]; [1]University of Louvain, Div. of Matls. & Process Engrg., Place Sainte-Barbe 2, Louvain-la-Neuve B-1348 Belgium; [2]IMEC, Inst. for Matls. Rsch. in Microelect., Wetenschapspark 1, Diepenbeek B-3590 Belgium

Electromigration drift studies on polycrystalline Blech-type test structures have been performed inside a scanning electron microscope. Based on the observed morphological evolution of the hillocking zone at the anodic end, a new analytical expression is presented for the length-dependence of the drift velocity by considering diffusional creep as the plastic flow mode involved in electromigration-induced hillocking. This expression is validated to the observed isothermal drift kinetics at the cathodic end. From the latter, a grain boundary grooving mechanism is proposed to account for the atomistic details of creep-controlled electromigration-induced motion, and the role of grain boundary structure in determining the local direction of groove propagation is illustrated.

4:05 PM
Work Hardening and High Ductility in High-Strength Electroplated Cu with Nanoscale Growth Twins: Y. Morris Wang[1]; *Evan Ma*[1]; Q. H. Lu[2]; M. L. Sui[2]; L. Lu[2]; K. Lu[2]; [1]Johns Hopkins University, Matls. Sci. & Engrg., Baltimore, MD 21218 USA; [2]Chinese Academy of Sciences, Inst. of Metal Rsch., Shenyang China

A high density of growth twins in pure Cu imparts high strength while preserving the room for efficient dislocation storage upon plastic deformation, leading to high strain hardening rates. Tensile test results at 77 K are used to illustrate these effects. In addition to exhibiting high yield strength, the material sustains significant work hardening rates to large strains and at high stress levels, reaching an ultrahigh (GPa) tensile strength combined with impressive uniform elongation and a tensile ductility ~30%. The nano-twinned microstructure is an interesting addition to the repertoire of nanostructured metals that offer a combination of both high strength and ductility.

4:20 PM
Investigation of Maximum Accumulated Plastic Strain Distribution During Equal-Channel Angular Pressing (ECAP), Using 2D and 3D FEM Modeling: *Vladimir S. Zhernakov*[1]; Igor N. Budilov[1]; Salavat T. Kusimov[1]; Igor V. Alexandrov[1]; [1]Ufa State Aviation Technical University, 12, K. Marx St., Ufa 450000 Russia

The current work presents the results of modeling of ECAP of pure copper by means of finite element method (FEM). The comparison of 2D and 3D modeling results was conducted to determine the accumulated plastic strain and its distribution along a billet volume. Stress-strain state of a copper billet after the first pass with constant strain rate was considered. It was established that the type of accumulated plastic deformation distribution in the center of the billet is practically similar in 2D and 3D models. However, 3D modeling allowed to estimate the distribution of deformation along the whole bulk billet and to establish the features of plastic flow heterogeneity during ECAP. The effect of both die design factors and friction on the accumulated plastic deformation was studied during 2D and 3D modeling. The obtained results are used for optimization of die-set parameters of ECAP.

4:35 PM Invited
Dislocation Behavior in Copper and Gold Thin Films: *John Balk*[1]; [1]University of Kentucky, Dept. of Cheml. & Matls. Engrg., 177 F. Paul Anderson Tower, Lexington, KY 40506 USA

The geometric constraints imposed by a metal thin film force dislocations to move differently than in a bulk metal. For film thicknesses on the order of one micron, threading dislocations channel between the substrate and film surface as they glide through a film. However, as the thickness of unpassivated films decreases below 400 nm, dislocations glide parallel to the film-substrate interface. This talk will cover various aspects of dislocation behavior in thin film systems, with an emphasis on unpassivated Cu and Au films. In-situ transmission electron microscopy observations will be used to explain the dislocation processes involved and will be related to models for thin film deformation. Parallel glide of dislocations, for instance, is a consequence of constrained diffusional creep. Although this creep mechanism dominates at high temperatures, TEM observations suggest that it persists down to room temperature. These and other aspects of thin film plasticity will be discussed.

5:00 PM
Micron-Scale Plasticity of Gold in the Absence of Strain Gradients: *Julia R. Greer*[1]; William D. Nix[1]; [1]Stanford University, Matls. Sci. & Engrg. Dept., 416 Escondido Mall, Bldg. Peterson 550, Stanford, CA 94305 USA

Classical laws of materials science dictate that mechanical behavior is independent of sample size, however recent experimental results display strong size effect at the microscale. During nanoindentation, non-uniformity of strains is responsible for indentation size effect. ISEs manifest themselves as apparent hardness increase at shallower depths and are explained by strain gradient plasticity theory. While this theory describes hardness variation for depths above ~100nm, it cannot predict discrete strain bursts characteristic of dislocation nucleation at shallower depths. Recently, atomistic behavior during mechanical deformation was studied via MD simulations and indicated that yield strength depended on sample size even without strain gradients. Experimental results testing plasticity of gold at nanoscale without strain gradients are presented. Methodology consists of two distinct fabrication processes of Au cylinders and their uniaxial compression. Test results indicate significant increase in flow stress to several GPa, near theoretical shear strength. Dislocation starvation model is proposed and discussed.

5:15 PM
Surfaces as Membranes: An Approach to Understanding Size Effects: *Danxu Du*[1]; David J. Srolovitz[1]; [1]Princeton University, Dept. of Mechl. & Aeros. Engrg., D214 E-Quad, Olden St., Princeton, NJ 08540 USA

The concept of a surface as an elastic membrane has been used to describe a wide range of mechanical effects, including interactions between steps on surfaces, growth stresses, etc. Such surface elastic membranes can induce significant stresses within small structures. On the other hand, descriptions of the deformation of small scale structures often require the introduction of strain gradient theories. In the present work, we attempt to connect these two, rather disparate concepts. The connection between the two comes from Stokes theorem that represents integrals over internal variables as lower dimension integrals over surfaces. We show how to rigorously go from a strain gradient theory description to a surface membrane description. The resultant formalism is much easier to implement numerically than the strain gradient formalism. This approach can be used for elasticity and plasticity problems. Applications to available experimental results will be discussed.

5:30 PM
Deformation Mechanisms of Microcrystalline and Nanocrystalline Ni Using Geometrically Different Indenters: *Reza A. Mirshams*[1]; Michael J. Kaufman[1]; [1]University of North Texas, Matls. Sci. & Engrg. Dept., PO Box 310440, Denton, TX 76203 USA

Hardness of electrodeposited nanocrystalline and commercially produced microcrystalline nickel were determined using three geometrically different indenter tips. The results indicate that the dislocation based model describes the deformation mechanism in microcrystalline nickel using the Berkovich tip. However, observations differ with other tips and for the nanocrystalline nickel. Microstructural

examination reveals different deformation mechanisms in the two materials with the different tips.

5:45 PM
Local Strain Development in Near Stoichiometric RuAl Alloys: *Aomin Wu*[1]; Tresa M. Pollock[1]; Qiang Feng[1]; Marc De Graef[2]; [1]University of Michigan, Dept. of Matls. Sci. & Engrg., Ann Arbor, MI 48109 USA; [2]Carnegie Mellon University, Dept. of Matls. Sci. & Engrg., Pittsburgh, PA 15213-3890 USA

RuAl intermetallics display unusual deformation characteristics compared to all other B2 intermetallics. Investigations on the evolution of strains within individual grains have been studied in near stoichiometric RuAl alloys by surface displacement mapping. Strain development is influenced by the amount and distribution of secondary ?Ô-Ru phase. Comparisons between Von Mises effective strain maps and Schmid factors suggest that enhanced straining coincides with a large Schmid factor for {110}<011> slip system, but not for {110}<001>, which is another available slip system in single phase RuAl. Results of dislocation studies using TEM foils prepared by Focus Ion Beam (FIB) on specific grains with representative strain concentrations will be presented. The varying influence of grain orientations, presence of multiple phases and the availability of different dislocation substructure on the overall strain development of RuAl will be evaluated.

Micromechanics of Advanced Materials II (Symposium in Honor of James C.M. Li's 80th Birthday): Impression and Indentation Testing

Sponsored by: Structural Materials Division, ASM International: Materials Science Critical Technology Sector, SMD-Mechanical Behavior of Materials-(Jt. ASM-MSCTS)
Program Organizers: Fuqian Yang, University of Kentucky, Department of Chemical and Materials Engineering, Lexington, KY 40506 USA; C. C. Chau, Pactiv Corporation, Canandaigua Technology Center, Canandaigua, NY 14424 USA; Sung Nee George Chu, Multiplex Inc, South Plainfield, NJ 07080 USA; M. Ashraf Imam, Naval Research Laboratory, Materials Science & Technology Division, Washington, DC 20375-5343 USA; Teh-Ming Kung, Eastman Kodak Company, Rochester, NY 14650 USA; Peter K. Liaw, University of Tennessee, Materials Science and Engineering, Knoxville, TN 37996-2200 USA; B. B. Rath, Naval Research Laboratory, Materials Science and Component Technology Directorate, Washington, DC 20375-5341 USA

Monday PM Room: 3000
February 14, 2005 Location: Moscone West Convention Center

Session Chairs: M. A. Imam, Naval Research Laboratory, Washington, DC 20375-5000 USA; T. G. Nieh, Livermore National Laboratory, Livermore, CA 94551-9900 USA

2:00 PM Invited
On Some Investigations With the Impression Creep Technique: *D. H. Sastry*[1]; [1]Indian Institute of Science, Metall., Bangalore India

The impression creep technique is a modified indentation creep test wherein the conical or ball indenter is replaced by a cylindrical, flat bottomed punch. It offers several advantages such as simplicity, small quantity of the sample, constant applied load resulting in a constant stress, stable deformation because of the absence of the tertiary creep stage, multiple testing on a single sample, suitability for application to brittle materials etc. This test, pioneered by Prof. Li, is extensively applied in this laboratory to investigate a variety of problems. This novel test technique has been first validated by conducting parallel tensile creep tests on a number of materials. The stress exponent for steady state creep rate, the activation area and the activation energy as determined from the impression creep data are found to concur with those estimated from tensile creep testing. The extent of deformation under the punch as well as the effect of punch diameter have been investigated. The test has been applied to identify the rate controlling mechanisms of creep at high temperatures in a number of metals and alloys. The technique has also been exploited to assess the "single crystal" creep behavior from a polycrystalline sample. Utilizing the impression creep test, the creep behavior of individual zones in stainless steel weldments has been established. The usefulness and the simplicity of the impression creep test have been further demonstrated by its application to the study of superplastic behavior in alloys. This paper presents a cross section of the results obtained in the above investigations. It is concluded that the impression creep test technique is capable of yielding much of the information that can be obtained from tensile creep testing, and furthermore, can provide data which are impossible or extremely difficult to obtain with conventional creep testing.

2:25 PM Invited
Indentation Test Methods: Progress and Accomplishments: *M. Ashraf Imam*[1]; Fahmy M. Haggag[2]; Heshmat A. Aglan[3]; Robert L. Bridges[4]; [1]Naval Research Laboratory, Matls. Sci. & Tech. Div., Code 6320, Washington, DC 20375-5343 USA; [2]Advanced Technology Corporation, 1066 Commerce Park Dr., Oak Ridge, TN 37830-8026 USA; [3]Tuskegee University, Tuskegee, AL USA; [4]Oak Ridge National Laboratory, 4BWXT Y-12, Oak Ridge, TN USA

Traditionally, investigations of elastic and plastic behavior of structural materials have been carried out by uniaxial loading of bars and by multiaxial loading of plates or thin-wall tubes. An alternative method is to use indentation testing techniques and determining the resulting geometric features of the indentation region for specific loadings. This approach offers significant advantages over the conventional method of testing. One method was first developed and demonstrated by J. C. M. Li and coworkers to study high temperature creep. Over the years, different shape and size of the indenters have been used and their applications have been extended to study elastic modulus, yield strength, strain-hardening exponent, strain-rate sensitivity and superplasticity of a wide range of materials including fatigue, stress relaxation, mechanical anisotropy and fracture toughness. In this report emphasis is given to Automated Ball Indentation (ABI) test techniques, invented in 1989, to measure key mechanical properties and its applications to aerospace, transportation, pipelines, shipyards, military, and nuclear.

2:50 PM Invited
Creep Characterization of Microelectronic Solder Balls Based on Miniaturized Impression Creep Testing: *Indranath Dutta*[1]; Deng Pan[1]; Susheel G. Jadhav[2]; [1]Naval Postgraduate School, Mechl. & Astronautl. Engrg., 700 Dyer Rd., Monterey, CA 93943 USA; [2]Intel Corporation, 5000 W. Chandler Blvd., MS CH5-165, Chandler, AZ 85226 USA

The technique of impression creep, first proposed by Professor Li in the 1970s, offers the ability to test specimens of very small material volumes within a relatively short time, and with minimal sample preparation. Here we report on the successful miniaturization and implementation of the impression creep approach to study the creep behavior of 750mm diameter ball grid array (BGA) solder balls attached to a microelectronics packaging substrate. The work was prompted by the strong interest in generating creep databases on lead-free solders based on life-sized joints, in response to the ongoing worldwide transition to lead-free solders in the microelectronics industry. In this paper, experimental creep results on Sn-4.0wt%Ag-0.5wt%Cu BGA balls will be presented, with emphasis on the role of microstructure on creep. Despite the many advantages of impression creep, its widespread utilization has been inhibited by the difficulties in converting impression creep data into a conventional creep equation. Here we report on a detailed finite element (FE) study, undertaken to establish an approach to determine the requisite conversion constants C and k (to translate impression velocity and punch stress to creep rate and uniaxial stress, respectively) as functions of material properties. By defining an appropriate gauge volume based on the crept zone under the impression punch, and by correlating the mean equivalent creep strain with the mean effective stress within this volume, one can arrive at suitable values of C and k, and obtain correlations between key material properties and these constants. Results of these ongoing efforts will be reported.

3:15 PM Invited
Deep Penetration Micro-Indentation Testing of Oriented Polypropylene: *D. M. Shinozaki*[1]; *J. Lo*[1]; [1]University of Western Ontario, Mechl. & Matls. Engrg., London, Ontario N6A 5B9 Canada

Displacement controlled deep penetration microindentation testing has been applied to uniaxially oriented polypropylene. The load-displacement measurements recorded showed differences from those reported in earlier work on isotropic polymers. Examination of the microstructure ahead of the tip face showed that the deformation mechanisms varied with orientation of the tip axis relative to the molecular axis of the material. In the case of penetration parallel to the orientation direction, distinct kink bands were observed ahead of the tip face, localized along the axis of penetration. The end-on indentation of uniaxially oriented polypropylene is shown to be reasonably modeled using a modified version of the Slaughter analysis, originally developed to describe compression of unidirectional fiber com-

posites. As expected, the constraint involved in microindentation testing is found to affect the measured load displacement curve.

3:40 PM Break

3:45 PM
Impression Creep of Sn-3.5 Ag Eutectic Alloy: Fuqian Yang[1]; *Lingling Peng*[1]; [1]University of Kentucky, Chem. & Matls. Engrg., Lexington, KY 40506 USA

The creep behavior of Sn-3.5Ag eutectic alloy was investigated by using impression test technique in the temperatures range 333-453 K and under a punching stress between 3.4 MPa at 453 K and 67.1 MPa at 333 K. The alloy was annealed for 10 hours at 473 K before the impression test. Using a power law between the steady-state impression velocity and the punching stress, the activation energy increases with the punching stress from 44.7 kJ/mole at 6.7 MPa to 79.2 kJ/mole at 46.9 MPa and the stress exponent changes from 1.03 (3.4-13.4 MPa) to 5.9 (20.1-40.2 MPa). However, by using a hyperbolic sine function between the steady-state impression velocity and the punching stress, a single activation energy is found to be 51.0 kJ/mole, which is close to the activation energy for grain boundary diffusion in pure Sn.[1] This suggests that a single mechanism such as grain boundary fluid flow could control the time-dependent plastic flow of Sn-3.5Ag eutectic alloy under the testing conditions. This research is s upported by NSF through a grant DMR-0211706 monitored by Drs. Guebre Tessema and Bruce A. MacDonald. [1]B. Okkerse, Acta. Metall. 2 (1954) 551.

4:10 PM Invited
Nanoindentation Tests for the Investigation of the Mechanical Properties of Bismuth Implanted Layered Amorphous Ge Film: Csilla Kadar[1]; Peter Tasnádi[1]; Gábor Petõ[2]; *András Juhász*[1]; [1]Eötvös University, Dept. for Gen. Physics, 1117 Pázmány Péter st.1/A, Budapest Hungary; [2]Research Institute for Technical Physics and Materials Science, Budapest Hungary

In an earlier paper (Juhász at al. Nucl. Instr. Methods in Phis. Res. B. 148. 1999 355-359.) preliminary results of microhardness measurements taken from bismuth implanted amorphous Ge film were presented. In this paper an account is given about the resumption of that work. The mechanical investigations were carried out by nanoindentation tester which provides more sensitive method than that used previously. The effect of the annealing applied after the implantation was also investigated. The hardness, the elastic modulus and the brittleness of the implanted samples were found significantly lower than those of the unimplanted material. Due to annealing the mechanical properties of the implanted samples were changed toward the unimplanted state. Mechanical measurements were completed by revealing the microstructure of the specimens by electron microscopy which showed the bubbled structure of the implanted zones. The results obtained for the implanted and annealed state are interpreted by a composite model concerning a layered structure consisting of weak (bubbled) and strong bands.

4:35 PM Invited
Relationships Between the Work of Indentation, Hardness, Elastic Modulus, and the Friction and Wear Behavior of Materials: Wangyang Ni[1]; Che-Min Cheng[2]; *Yang-Tse Cheng*[1]; [1]General Motors Research and Development Center, Matls. & Processes Lab., MS 480-106-224, 30500 Mound Rd., Warren, MI 48090 USA; [2]Institute of Mechanics, State Key Lab. for Nonlinear Mech., Beijing 100080 China

The work of indentation is examined using dimensional analysis and finite element calculations for conical and spherical indentation in homogeneous solids and for conical indentation in thin films on substrates. For conical indentation in elastic-plastic solids with work-hardening, we established a relationship between the ratio of hardness to elastic modulus and the ratio of irreversible work to total work of indentation.[1,2] Using this relationship, the ratio of hardness to elastic modulus can be obtained directly from measuring the work of indentation for homogeneous solids. For spherical indentation in elastic-plastic solids with work hardening, we found simple relationships between hardness, reduced modulus, indentation depth, indenter radius, and work of indentation.[3] We have also uncovered similar relationships for conical indentation in hard films on soft substrates. These relationships, together with the relationship between initial unloading stiffness and reduced modulus, provide an energy-based method for determining contact area, reduced modulus, and hardness of materials from instrumented indentation measurements using conical, pyramidal, and spherical indenters. Finally, we show that the ratio of irreversible work to total work plays an important role in determining the friction coefficient and wear behavior of materials and suggest a strategy for reducing friction and enhancing wear resistance of materials. [1]Y.-T. Cheng and C.-M. Cheng, Appl. Phys. Lett. 73, 614 (1998). [2]Y.-T. Cheng, Z. Li, and C.-M. Cheng, Phil. Mag A 82, 1821 (2002). [3]W. Ni, Y.-T. Cheng, C.-M. Cheng, and D. S. Grummon, J. Mat. Res. 19, 149 (2004).

5:00 PM Invited
Elastic Deformation Due to Oscillating Indentations: B. B. Rath[2]; *H. Y. Yu*[1]; [1]US Army Asian Research Office, Tokyo Japan; [2]Naval Research Laboratory, Washington, DC USA

Recent developments in instrumented indentation include the use of dynamic oscillation for improved sensitivity and testing capabilities. Instrumented indentation, also known as depth-sensing indentation or nano-indentation, is increasingly being used to probe the mechanical response of metals, ceramics, polymers and biological materials. Dynamic contact problems have also received considerable attention recently in the mathematical literature. This work is to study the elastic field in an isotropic half space due to dynamic frictionless indentation. The rigid indenter tip is assumed to be axisymmetric with a smooth convex profile such that the contact area is a circular region. A point load method will be used to obtain the analytical solutions for the time-harmonic normal indentation.

5:25 PM Invited
Plasticity of Single Crystals Under a Sliding Indenter: *Bhaskar S. Majumdar*[1]; Bing Ye[1]; [1]New Mexico Tech, Dept. of Matls. & Metallurgl. Engrg., Socorro, NM 87801 USA

While the literature on the friction and wear of metallic materials is voluminous, there are still considerable questions regarding the deformation and damage mechanisms. The near surface behavior is dominated by plasticity and microstructural evolution, and these in turn dictate frictional forces and further wear. Such near surface phenomenon have taken on added importance in modern micro electro mechanical systems that employ textured metallic films. In this work, we have focused attention on single crystal substrates, with a view to understanding fundamental dislocation processes under a sliding indenter. The results indicate a very strong influence of the orientation of loading on the deformation response, and this appears to be manifested mainly through the hardening response. The geometry of multiple slip and the morphology of deformation will be illustrated and compared with available data in the literature on highly textured fcc alloys. The effects of friction coefficients are analyzed, and we comment on how the morphology of slip might in turn influence frictional coefficients. The first author had the privilege of learning plasticity and dislocation theory from Professor Li, and provides his respects on the occasion of his 80th Birthday.

5:50 PM
Indentation Studies of Self Adhesion of Poly(dimethylsiloxane): *Xinzhong Zhang*[1]; Fuqian Yang[1]; J. C.M. Li[1]; [1]University of Rochester, Mechl. Engrg., Rochester, NY 14627 USA

The self-adhesion of poly(dimethylsiloxane) (PDMS) was studied using a cylindrical indenter. The indenter had a flat end coated with a thin layer of PDMS. The flat end was contacting the planar surface of a PDMS block. Unlike spherical indenters, there was no hysteresis in loading and unloading in the elastic range since the contact area did not vary. The pull-off force is a measure of the energy of self adhesion at the instant of separation. The self-adhesion energy between PDMS surfaces was found to increase with the square root of contact time indicating molecular diffusion as the dominant mechanism for self-adhesion. The activation energy for self diffusion of PDMS was obtained from the temperature effect and was compared with that of viscous flow of PDMS measured by an impression creep test. Work supported by NSF through DMR-9623808 monitored by Bruce MacDonald.

Microstructural Processes in Irradiated Materials: Modelling Defect Evolution and Oxide Dispersion Strengthened Alloys

Sponsored by: Structural Materials Division, SMD-Nuclear Materials Committee-(Jt. ASM-MSCTS)
Program Organizers: Brian D. Wirth, University of California, Department of Nuclear Engineering, Berkeley, CA 94720-1730 USA; Charlotte S. Becquart, Ecole Nationale Superieure de Chimie de Lille, Laboratoire de Metallurgie Physique et Genie des Materiaux, Villeneuve d'Ascq cedex 59655 France; Hideki Matsui, Tohoku University, Institute for Materials Research Japan; Lance L. Snead, Oak Ridge National Laboratory, Metals and Ceramics Division, Oak Ridge, TN 37830-6138 USA

Monday PM Room: 3011
February 14, 2005 Location: Moscone West Convention Center

Session Chairs: Christophe Domain, EDF R&D, Dept. MMC, Les Renardieres, Moret sur Loing F-77250 France; Brian Wirth, University of California, Nucl. Engrg. Dept., Berkeley, CA 94720-1730 USA

2:00 PM Invited
Temperature Accelerated Dynamics Study of Radiation Damage Annealing in MgO: *Arthur F. Voter*[1]; [1]Los Alamos National Laboratory, Theoretl. Div., T-12, MS B268, Los Alamos, NM 87545 USA

We present results of a collaborative[1] atomistic study of radiation damage annealing in MgO following cascades in the 1 keV energy range. Using a Buckingham potential, knock-on events were simulated with molecular dynamics. Longer times were probed using temperature accelerated dynamics, enhanced by minimum escape barriers from dimer searches (dimer-TAD). Configurations with a small number of defects, representative of the post-cascade results, were evolved using dimer-TAD for times up to seconds and beyond. Results were complimented with molecular statics and some verified with density functional theory. An interesting picture emerges for the diffusion and coalescence of defects produced in this energy range, involving time scales from ns to years. Also, diffusion of interstitial clusters shows a surprising nonmonotonicity. [1]B.P. Uberuaga, R. Smith, A.R. Cleave, F. Montalenti, G. Henkelman, R.W. Grimes, A.F. Voter, and K.E. Sickafus, Phys. Rev. Lett. 92, 115505 (2004).

2:40 PM Invited
Kinetic Monte Carlo Calculations to Study Defect Evolution in Irradiated Metals: *Maria J. Caturla*[1]; [1]Universidad de Alicante, Fisica Aplicada, Facultad de Ciencias, Fase II, Alicante E-03690 Spain

Currently kinetic Monte Carlo (kMC) models are widely used to study the accumulation and evolution of damage during irradiation. In this talk we will give a brief overview on the calculations done for pure metals, both f.c.c. and b.c.c. The influence of different parameters in the final conclusions of the simulations will be discussed. In particular we will describe the use of kMC models to understand the relevant parameters that control microstructure evolution during irradiation. Emphasis will be made in those parameters where little or no information exists form either experiments or simulations, such as the interaction of defects with impurities. One important part of the presentation will be devoted to He effects in b.c.c. Fe comparing it to f.c.c. metals and to experiments both on He desorption and neutron irradiation.

3:20 PM
Displacement Cascade Influence on Void and Precipitate Nucleation: *Kenneth Calvin Russell*[1]; Byungkon Kim[1]; [1]Massachusetts Institute of Technology, Dept. Matl. Sci. & Engrg. & Nucl. Engrg., Rm. 13-5050, 77 Mass. Ave., Cambridge, MA 02139-4307 USA

Displacement cascades are the primary damage event in most irradiation of metals. The cascades are typically vacancy-rich regions surrounded by a halo of self-interstitial atoms. At reactor operating temperatures the vacancy is mobile and the cascades dissipate to create a more or less uniform sea of vacancies and self-interstitial atoms. This excess of point defects gives greatly enhanced diffusion rates and in addition provides a driving force for nucleation, in particular of voids, dislocation loops, and precipitate particles. The cascades may also have direct effects on nucleation by either creating on destroying embryos of nucleating aggregates. A partial differential equation for nucleation is derived which includes such effects. The equation is normalized to give dimensionless coefficients of the derivatives, which in turn predict experimental conditions when the various cascade effects will and will not be significant. More complete solutions of the differential equation will also be presented.

3:40 PM Break

4:10 PM Invited
Development of Advanced Nanostructured Ferritic Alloys for Nuclear Fission and Fusion Applications: *David T. Hoelzer*[1]; Matt J. Allinger[2]; Michael K. Miller[1]; G. R. Odette[2]; Jim Bentley[1]; [1]Oak Ridge National Laboratory, Metals & Ceram. Div., Oak Ridge, TN 37831 USA; [2]University of California, Santa Barbara, CA 93106 USA

Mechanically alloyed (MA) oxide-dispersion strengthened 12-14Cr ferritic alloys, such as the Japanese 12YWT and INCO MA957, contain a high number density of <5nm sized particles enriched in Y, Ti, and O. The superior high-temperature creep properties of these so-called nanostructured ferritic alloys (NFAs) are attributed to this nano-particle dispersion. In addition, since their unique microstructure may also provide enhanced resistance to radiation damage and high levels of transmutation product helium, both the fusion and advanced fission reactor materials programs have considerable interest in NFAs. This paper highlights our current experimental and theoretical understanding of the nano-particle structure and formation and strengthening mechanisms, including the effects of processing variables, as well as their high temperature stability. Potential issues such as costs, joining methods, their stability under irradiation and low fracture toughness will also be discussed briefly.

4:50 PM
Microstructural Analysis on Tensile-Deformation Behavior of Oxide-Dispersion Strengthened Ferritic Steels: *Ryuta Kasada*[1]; Naoki Toda[2]; Akihiko Kimura[1]; [1]Kyoto University, Inst. of Advd. Energy, Gokasho, Uji, Kyoto 611-0011 Japan; [2]Kyoto University, Grad. Sch. of Energy Sci., Gokasho, Uji, Kyoto 611-0011 Japan

For high burn-up operation of light water reactor and super critical water reactor, our research group has been developing a series of oxide dispersion strengthening (ODS) ferritic steels as fuel cladding because of the excellent high-temperature strength and resistance to irradiation hardening.[1] These excellent performances are considered to be due to the ultra-fine nano-scale yttria particles dispersed in the matrix. Although the strengthening mechanism due to the yttria dispersoids has been considered to be the Orowan bypassing mechanism, no obvious evidence was shown for the ODS steels containing such ultra-fine dispesoids. In this study, deformed microstructure of the ODS steels was investigated and discussed. The materials used were ODS ferritic steels which contain various chromium contents of 13~22wt%.[1] TEM bservations were carried out with post- and in-situ straining techniques. [1]A. Kimura, et al., "R&D of Advanced Ferritic Steel for High Burn-up Fuel Cladding", ICAPP'04, in press.

5:10 PM
Tensile Properties and Fracture Mode of a Wrought ODS Molybdenum Sheet Following Fast Neutron Irradiation at Temperatures Ranging from 300C to 1000C: *Brian V. Cockeram*[1]; Richard W. Smith[1]; Lance L. Snead[2]; [1]Bechtel Bettis Laboratory, PO Box 79, ZAP 05R/MT, W. Mifflin, PA 15122-0079 USA; [2]Oak Ridge National Laboratory, Metals & Ceram. Div., Oak Ridge, TN 37831-6138 USA

A commercially available Oxide Dispersion Strengthened (ODS) Molybdenum alloy that has been rolled into 0.76 mm thick sheet possesses a fine dispersion of La-oxide particles, fine grain size (about 1.2 um), and a high recrystallization temperature (1800C). These microstructural features result in excellent creep resistance and strength at high temperatures, and high levels of tensile elongation at low temperatures. Since wrought processing results in alignment of oxide particles in the working direction, the mechanical properties of ODS molybdenum are anisotropic, but are generally an improvement over many molybdenum-base alloys. The microstructural features of ODS moylbdenum that improve the non-irradiated mechanical properties may also have an influence on the irradiated properties. The change in the mechanical properties of ODS molybdenum after irradiation are not known, and are investigated herein following irradiation in the High Flux Isotope Reactor (HFIR) at 300C, 600C, and 870C to 1000C to neutron fluences between 10.5 to 200 X 10^20 n/cm^2 (E > 0.1 MeV). Irradiation of ODS molybdenum at 600C resulted in a large increase in strength (137% to 56%), but the Ductile to Brittle Transition Temperature (DBTT) was room-temperature. The room-temperature DBTT for ODS is below the range of DBTT values (100C to 710C) reported in literature for molybdenum alloys irradiated at 600C, which demonstrates that ODS molybdenum has an improved level of resistance to radiation embrittlement. The thin sheet toughening mechanism, where ODS molybdenum splits along grain boundaries during

fracture to leave thin ligaments that are stretched under plane stress conditions to large amounts of elongation, is shown to produce the ductile behavior at room-temperature. However, irradiation of ODS molybdenum at 300C resulted in a large amount of strengthening (150% to 130%) and the DBTT (800C) that is the same as observed for unalloyed molybdenum. Irradiation of ODS at 870C to 1000C resulted in small increases in yield strength (29% to 10%) with a post-irradiated DBTT (-100C) that is lower than values reported in literature for molybdenum alloys. Fractography and microstructure examinations are used to show that a fine grain size and fine oxide particle size provide the observed improvements in the post-irradiated tensile properties of ODS molybdenum.

Multicomponent Multiphase Diffusion Symposium in Honor of John E. Morral: Analysis of Interdiffusion Microstructures: Session II

Sponsored by: Materials Processing & Manufacturing Division, Structural Materials Division, EMPMD/SMD-Alloy Phases Committee, MPMD-Solidification Committee, ASM/MSCTS-Atomic Transport Committee

Program Organizers: Carelyn E. Campbell, National Institute of Standards and Technology, Metallurgy Division, Gaithersburg, MD 20899-8555 USA; Ursula R. Kattner, National Institute of Standards and Technology, Metallurgy Division, Gaithersburg, MD 20899-8555 USA; Afina Lupulescu, Rensselaer Polytechnic Institute, Materials Science & Engineering, Troy, NY 12180-3590 USA; Yongho Sohn, University of Central Florida, Advanced Materials Processing & Analysis Center and Mechanical, Materials and Aerospace Engineering, Orlando, FL 32816-2455 USA

Monday PM Room: 3007
February 14, 2005 Location: Moscone West Convention Center

Session Chairs: John H. Perepezko, University of Wisconsin, Matls. Sci. & Engrg., Madison, WI 53706 USA; Harold D. Brody, University of Connecticut, Matls. Sci. & Engrg., Storrs, CT 06169-3136 USA

2:00 PM Invited
A Model for the Lateral Deformation of Diffusion Couples: *W. J. Boettinger*[1]; G. B. McFadden[1]; S. R. Coriell[1]; J. A. Warren[1]; R. F. Sekerka[2]; [1]NIST, Gaithersburg, MD 20899 USA; [2]Carnegie-Mellon University, Pittsburgh, PA 15213 USA

A model is proposed to describe the shape change of a binary diffusion couple when the intrinsic (lattice) diffusivities of the two substitutional species differ. The classical uniaxial Kirkendall shift is obtained only if the displacements are artificially constrained to be in the diffusion direction. In the usual experimental case when the lateral surfaces of the diffusion couple are traction-free, a more general displacement field is obtained that accounts for the lateral shape change data of Voight and Ruth. In the interdiffusion zone, near the free surfaces of the diffusion couple, the sample deforms inward and outward respectively on opposite sides of the couple. The model uses an isotropic stress-free strain rate proportional to the vacancy creation/annihilation rate and an elastic/plastic constitutive model. In addition to numerical simulations with the model, the limiting behaviors for couples with lateral dimensions large and small compared to the diffusion distance are reported.

2:30 PM Invited
Teaching the Square-Root Diffusivity Method: *Martin Eden Glicksman*[1]; Afina Lupulescu[1]; [1]Rensselaer Polytechnic Institute, Matls. Sci. & Engrg., Troy, NY 12180 USA

The interdiffusion of atomic species in multicomponent alloys is a subject of considerable complexity, with broad applications throughout materials engineering. Specifically, multicomponent diffusion concepts provide novel design strategies to improve the performance of alloys and coatings that must resist degradation and aging at elevated temperatures. Engineers who conceive and design structures for high-temperature use are challenged by these problems. Consequently, during their undergraduate or graduate programs, materials engineering students should be exposed to fundamental aspects of multicomponent diffusion. Professor John Morral demonstrated the utility of a related transport matrix, the "square-root diffusivity matrix." His integrative methodology to understand many aspects of multicomponent diffusion, now taught at Rensselaer, employs his computer program, Profiler. Through this approach, students are now easily acquainted with one-dimensional, single-phase, multicomponent diffusion problems as a tractable class of numerical solutions, including the formation of zero-flux planes, up-hill diffusion, S-shaped diffusion paths, etc.

3:00 PM
Implementing the Square-Root Diffusivity Method: *Afina Lupulescu*[1]; Martin Eden Glicksman[1]; Srividya Kailasam[2]; [1]Rensselaer Polytechnic Institute, Matls. Sci. & Engrg., Troy, NY 12180 USA; [2]National Exposure Research Laboratory, Las Vegas, NV 89119 USA

Applying the theory of multicomponent diffusion and solving Fick's second law is a challenging task. Fortunately, most of the tedious mathematical labor can be eliminated by employing programs that efficiently handle the required linear algebra steps. In 1986, Morral and Thompson developed a systematic methodology for constructing one-dimensional single-phase multicomponent diffusion solutions, referred to as the "square-root diffusivity method." Implementing the Morral-Thompson method for multicomponent alloys is now made convenient by using the public domain computer program, Profiler, developed by Morral. Quantitative predictions of multicomponent diffusion effects, particularly the penetration curves and diffusion paths, were checked against experiments using several programs. Generally, good results were obtained. To study multicomponent diffusion behavior for different alloys and investigate the kinetics of zero-flux planes (ZFP's), the authors developed a new MatLab© code that closely follows a combination of Morral and Thompson's approach as well as that by Glicksman and Lupulescu.

3:25 PM Break

3:40 PM
Test of Darken's Mobility Assumption in the Cu-Ni-Zn System: *Robert Thomas DeHoff*[1]; Nagraj S. Kulkarni[2]; [1]University of Florida, Matls. Sci. & Engrg., Gainesville, FL 32611 USA; [2]Oak Ridge National Laboratory, Metals & Ceram. Div., Bldg. 4515, #111, Oak Ridge, TN 37831-6063 USA

Darken's assumption that the mobility of a component in a homogenous system is the same as that in a system subjected to a composition gradient was central in establishing relations between the tracer and intrinsic or interdiffusion coefficients. These relations have been examined primarily in binary systems with mixed results. In this presentation, the Darken relations are examined for the ternary Cu-Ni-Zn system for which adequate tracer diffusion data and CALPHAD-based thermodynamic models are available. With the aid of an intrinsic diffusion simulation developed by the authors, the composition paths and Kirkendall shifts predicted from the Darken and Manning theories are compared with experimental data. Important issues concerning the development of multicomponent diffusion databases are addressed.

4:05 PM
Flux-Independent Theory of Nonlinear Diffusion for Vegard's Law Solutions: *J. S. Kirkaldy*[1]; [1]McMaster University, Brockhouse Inst. for Matls. Rsch., 1280 Main St. W., Hamilton, Ontario L8S 4M1 Canada

While the phenomenological Boltzmann-Matano (B-M) analysis argues that a concentration-dependent diffusion coefficient D(X) relates to infinite diffusion couple experiments by the solute-conserving, flux-formulated non-linear parabolic equation in terms of mole fraction X, $-(1/2)(dX/d\lambda)=d/(d\lambda)\ D(X)\ (dX/d\lambda)$, this contribution proves that for stable substitutional Vegard's Law solutions, automatically subsuming a mechanistic vacancy-dominated contribution to a Kirkendall creep process at local equilibrium, both a crystalline volume and a molar mass conserving condition follow. Concomitantly, the usual Onsager generalization from irreversible thermodynamics leading to this equations has to be replaced by a Helmholz free energy based on a Ginzburg-Laudau variational equation in which a solute-conserving flux does not and cannot enter under threat of over-determination. Consequently, conservation is relegated to the processing and symmetry of the free energy density whereby D(X) proves to reside outside the differentials on the right. As further validation of the flux-free construction it is demonstrated that in contrast to the above B-M formulation the variable D's extracted from diffusion couples is approximate to those generated by a set of incremental couples where consistently D also resides outside the differentials. The simplification of the B-M analysis and the methodology for a correctly framed coefficient evaluation are then established. Since in the ternary generalization solute fluxes are likewise not defined, the concept of "zero flux plane" must be re-examined. It is remarkable that in this representation the commonly observed single clustering maxim act as Kirkendall drift markers. Furthermore, in this Vegard's Law formulation volume and mole numbers remain conserved as in the binary case, their neutral

planes are not coincident. A quantitative verification of the flux-free disposition is given for the representative cases.

Neutron Diffraction Characterization of Mechanical Behavior: Deformation I

Sponsored by: ASM International: Materials Science Critical Technology Sector, Structural Materials Division, SMD-Mechanical Behavior of Materials-(Jt. ASM-MSCTS)
Program Organizers: Hahn Choo, University of Tennessee, Department of Materials Science and Engineering, Knoxville, TN 37996 USA; Camden R. Hubbard, Oak Ridge National Laboratory, Metals and Ceramics Division, Oak Ridge, TN 37831 USA; Peter K. Liaw, University of Tennessee, Materials Science and Engineering, Knoxville, TN 37996-2200 USA; Xunli Wang, Oak Ridge National Laboratory, Spallation Neutron Source, Oak Ridge, TN 37831 USA

Monday PM Room: 3004
February 14, 2005 Location: Moscone West Convention Center

Session Chairs: Camden R. Hubbard, Oak Ridge National Laboratory, Metals & Ceram. Div., Oak Ridge, TN 37831 USA; Xunli Wang, Oak Ridge National Laboratory, Spallation Neutron Source, Oak Ridge, TN 37831 USA

2:00 PM Invited
Using Polycrystal Models and Neutron Diffraction to Advance Our Understanding of Materials: *Carlos N. Tomé*[1]; [1]Los Alamos National Laboratory, Matls. Sci. & Tech., MST-8, MS G755, Los Alamos, NM 87545 USA

Twinning is an important deformation mode in HCP materials, which strongly influences texture and hardening evolution during plastic forming. As a consequence, twinning contribution to texture and hardening has to be accounted for in constitutive descriptions of HCP aggregates. We use a Composite-Grain Polycrystal Model for describing twinning-related constitutive response in a general manner. This model accounts for directional barriers to dislocation motion posed by the twin lamellae in the grains, and also for the evolution of twin fraction with deformation in the grains. As an application, we simulate in-plane and through-thickness compression in rolled Zr, Be and Mg. Development of polycrystal models hinges strongly on the experimental capability for correlating modeling parameters with measurements. The neutron diffractometers SMARTS and HIPPO (LANSCE-LANL) have in situ testing capabilities, and provide us with an important tool for following evolution of texture, hardening and internal stresses as a function of deformation. We will discuss the results of our modeling efforts, related experimental results, and also how the experimental information can be used to infer information about microscopic deformation mechanisms.

2:20 PM
Coupling of Twinning, Texture, and Hardening During Deformation of Zirconium: *George C. Kaschner*[1]; Carlos N. Tomé[1]; Sven C. Vogel[2]; Don W. Brown[1]; [1]Los Alamos National Laboratory, MST-8, MS G755, Los Alamos, NM 87545 USA; [2]Los Alamos National Laboratory, LANSCE-12, MS H805, Los Alamos, NM 87545 USA

We present experimental observations of high purity zirconium loaded to small strains at quasi-static strain rates in an equilibrium liquid nitrogen bath then reloaded at room temperature. Neutron texture measurements were performed on each sample at three stages: as-annealed, after cryo-loading, and after room temperature deformation. Material loaded first in an in-plane orientation was found to harden compared to a reference test performed at room temperature only. Zirconium loaded first in the through-thickness orientation was found to soften when reloaded at room temperature compared to a room temperature reference test of the same orientation.

2:40 PM
Neutron Diffraction Study of Deformation Mechanisms of Magnesium Alloy AZ31: *Sean R. Agnew*[1]; D. W. Brown[2]; Ozgur Duygulu[1]; C. N. Tomé[2]; [1]University of Virginia, Matls. Sci. & Engrg., Charlottesville, VA 22904 USA; [2]Los Alamos National Laboratory, MTS-8, Los Alamos, NM USA

In-situ neutron diffraction experiments are performed on magnesium alloy AZ31 with a number of distinct initial textures resulting from prior hot-rolling, extrusion and equal channel angular extrusion. Diffraction is used to probe the development of internal stresses during loading and unloading. The anisotropy and asymmetry resulting from the individual textures is probed by testing in tension and compression along multiple sample directions. Not only are there striking distinctions in the mechanical behaviors of the variously textured samples, the internal stress development is quite distinct between the samples. The differences in the internal stress (and texture) development can be used to determine the active deformation mechanisms, in particular for deformation twinning. The determination of active mechanisms may be done in a more quantitative fashion for cases of slip dominated deformation through computer simulation of the internal stress development using the elastoplastic self-consistent (EPSC) code. Recently, a single set of critical resolved shear stress and hardening parameters have been used to simulate the observed mechanical behavior and internal stress developments of all the variously textured samples. Finally, samples are tested in-situ at elevated temperatures in order to determine if the internal stress development (i.e., deformation mechanisms) change with temperature.

3:00 PM
Three Dimensional Measurement of Type 2 Strains in Zircaloy-2: *Richard Alan Holt*[1]; Ronald Rogge[2]; Feng Xu[1]; Brian W. Leitch[3]; [1]Queen's University, Mechl. & Matls. Engrg., Kingston, Ontario K7L 3N6 Canada; [2]National Reserach Council of Canada, Neutron Prog. for Matls. Sci., Chalk River, Ontario K0J 1J0 Canada; [3]Atomic Energy of Canada Ltd., Chalk River Labs., Chalk River, Ontario K0J 1J0 Canada

The development of Type 2 residual strains has been measured in three dimensions in tensile specimens machined in the normal, transverse and rolling directions of hot-rolled Zircaloy-2 slab. The slab was about 25 cm wide by 3.8 cm thick by 200cm long. The texture of the slab and its spacial distribution were measured on the E3 spectrometer at the NRU reactor and the type two strains were measured in-situ during testing at room temperature in the L3 spectrometer using several crystallographic reflections. The (0002) plane normals were oriented predominently in the normal direction of the slab and was fairly uniform over about 2 cm at mid-thickness over most of the width of the slab. The tensile specimens were centered at mid-wall of the slab. Specimens tested in the transverse and rolling directions deformed by slip, and specimens tested in the normal direction eventually deformed by twinning. Strain measurements were made with and without load in the elastic regime and at intervals of 0.2-2% plastic strain after yield had occurred. The results are compared with the predictions of published self-consistant polycrystalline models.

3:20 PM
In-Situ Neutron Study of Deformation Mechanisms in Zirconium Alloys at Cryogenic and Room Temperatures: *T. A. Sisneros*[1]; M. A.M. Bourke[1]; D. W. Brown[1]; T. M. Holden[2]; S. C. Vogel[1]; T. R. Woodruff[3]; [1]Los Alamos National Laboratory, Los Alamos, NM USA; [2]Northern Stress Technologies, Deep River Canada; [3]University of Central Florida, Orlando, FL 32816 USA

In hexagonal metals, multiple slip and twinning systems compete as active deformation mechanisms. In particular, the formation of twins, plays an important role in the evolution of hardening by creating barriers to the propagation of dislocations for slip and other twin systems. The relative propensity of each deformation mechanism depends on parameters such as temperature, strain rate, purity, grain size, and texture. We report the effect of temperature variation (300K, 250K, and 216K) on twinning during a quasi-static uniaxial compression test in a zirconium alloy (Zr-1. 4Sn-0.1Cr-0Fe-0.1O-0.05Ni wt. %). The relative activities of the deformation mechanisms are determined by complementing in-situ neutron diffraction measurements performed at Los Alamos National Laboratory with polycrystalline plasticity modeling.

3:40 PM Break

4:00 PM Invited
Recents Developments in Diffraction Techniques for the Biomaterials: *Lodini Alain*[1]; [1]Universite de Reims, Moulin de la Housse, 51100 Reims France

The preferred orientation of hydoxyapatite crystallites at the interface bone-implant in sheep tibia bones has been measured with the neutron 2 axis diffractometer at the Institut Max Von Laue Paul langevin, extracted 60 days after implantation. The implant has two faces, one coated and one non-coated with plasma-sprayed HAp (80 microns). We probed the samples with a spatial resolution of 0.5 mm started from the interface in order to inspect the reorganisation of the HAp crystallite distribution after implantation.

4:20 PM Invited
Neutron Texture Analyses in Sauropod Bones: *A. Pyzalla*[1]; R. Ferreyro[1]; M. Stempniewicz[1]; A. Gunther[2]; H.-G. Brokmeier[2]; [1]TU Wien, Inst. of Matl. Sci. & Tech., Wien Austria; [2]GKSS, Geesthacht Germany

Sauropod dinosaurs are the largest animals that ever walked on earth. Their only remnants are fossilized bones. These fossilized bones due to their original complex hierarchical structure and due to diagenesis during burial have a complex multiphase microstructure. Within this microstructure part of the original features of the bone are preserved. The aim of our investigations is a comparison between the fossilized sauropod bones and contemporary animal bone. By this comparison we expect to find out how the extraordinary weight of the sauropods (up to 100 tons) was accommodated by the skeleton and specifically if the sauropod bone microstructure shows adaptations to the huge loads the bones had to carry. On of the strengthening mechanisms of bone is the development of a preferred orientation of the hydroxylapatite crystals. In order to verify the hypotheses that sauropod bones adapted to high loads by developing texture, neutron pole figure analyses were carried out at the diffractometer TEX-2 at GKSS, Geesthacht for femur and humerus of different sauropod species and animals of different ontogenetical age. The results of the analyses revealed that the fossilized bones still contain a fibre texture whose intensity varies across the bone diameter and differs for animals of different ontogenetical age. Even for animals of the same species and similar ontogenetical age the pole figures, in accordance with bone histology, imply different growth strategies for the long bones.

4:40 PM
Measurements and Predictions of Strain Pole Figures for Uniaxially Compressed Stainless Steel: *Cecilia Larsson*[1]; Bjorn Clausen[2]; Tom M. Holden[2]; Mark A.M. Bourke[2]; [1]Linkoping University, Dept. of Mechl. Engrg., Linkoping Sweden; [2]Los Alamos National Laboratory, Los Alamos, NM USA

Strain pole figures representative of residual intergranular strains were determined from an -2.98% uniaxially compressed austenitic stainless steel sample. The measurements were made using neutron diffraction on the Spectrometer for Materials Research at Temperature and Stress (SMARTS) at Los Alamos National Laboratory, using an Euler cradle to obtain spectra over a range of sample orientations. The time-of-flight technique used in SMARTS facilitated the simultaneous recording of eight hkl lattice plane reflections in individual spectra. The measurements were compared with predictions from an elasto-plastic self-consistent model and found to be in good agreement. The average of the strain differences between measurement and model for the angles and reflections considered was 17 x 10^{-6}, well within the error of 150 x 10^{-6} attributed to the measurement technique. The model was used to assess the sensitivity of the strain distribution in the deformed sample to the initial texture. While weak textures (such as the sample's 1.6 x random) did not show significant effects, stronger textures (e.g., 6 x random) reduced the inherent rotational symmetry of the strain field with strain variations of up to 900 x 10^{-6}.

5:00 PM
Crystallographic Texture and High Temperature Deformation Mechanisms in Zr-2.5Nb: *Richard Alan Holt*[1]; Pingshun Zhao[1]; Yue Li[1]; [1]Queen's University, Mechl. & Matls. Engrg., Kingston, Ontario K7L 3N6 Canada

The bulk crystallographic texture and through its wall variations in Zr-2.5Nb tubes extruded in the temperature range 650-975°C have been measured by neutron diffraction. The micro-texture and microstructure have also been characterized by scanning electron microscopy with electron backscattering diffraction and by transmission electron microscopy with selected area diffraction. At low extrusion temperature (650°C), where the majority phase is the hcp alpha-phase, the texture development is dominated by slip within the hcp phase, and in the courser grains the (0002) texture is predominantly radial - more so on the inside third of the tube wall where the strain ratio, Q, (the ratio of the radial to tangential strain during extrusion) is highest. At intermediate extrusion temperature (815°C), the texture development appears to be dominated by the interaction between the soft bcc beta-phase and the harder hcp phase which are present in roughly equal proportions. Boundary sliding mechanisms may be dominant. Here the (0002) texture is predominantly transverse, more so on the inside third of the tube wall. This clearly illustrates the change in deformation mechanisms from the lower temperature. Tubes made from billets pre-heated to 975°C, exhibited a large front to back variation, indicating substantial chilling during extrusion. The fronts of these tubes (the end exiting the extrusion press first) exhibited a beta-to-alpha transformation texture, with a dominant component of (0002) along the tube axis. The back ends exhibited a texture similar to that produced at 815°C because of chilling of the billet in the extrusion chamber. In the former case, the through wall variations corresponded to the temperature profile through the wall during extrusion, with the outer third of the wall (chilled by the container) exhibiting less of the transformation texture. A variety of microstructures are observed by SEM and TEM which correlate with the starting microstructures of the billets and with the observed textures.

Phase Stability, Phase Transformation and Reactive Phase Formation in Electronic Materials IV: Thin Film Stability and Reactions, Electro- and Thermomigration Phenomena

Sponsored by: Electronic, Magnetic & Photonic Materials Division, Structural Materials Division, EMPMD/SMD-Alloy Phases Committee

Program Organizers: Douglas J. Swenson, Michigan Technological University, Department of Materials Science & Engineering, Houghton, MI 49931 USA; Srinivas Chada, Jabil Circuit, Inc., FAR Lab/Advanced Manufacturing Technology, St. Petersburg, FL 33716 USA; Sinn-Wen Chen, National Tsing-Hua University, Department of Chemical Engineering, Hsinchu 300 Taiwan; C. Robert Kao, National Central University, Department of Chemical and Materials Engineering, Chungli City 32054 Taiwan; Hyuck Mo Lee, Korea Advanced Institute of Science & Technology, Department of Materials Science & Engineering, Taejon 305-701 Korea; Suzanne E. Mohney, Pennsylvania State University, Department of Materials Science & Engineering, University Park, PA 16802 USA; Katsuaki Suganuma, Osaka University, Department of Nanomaterials and Environmental Conscious Technology, Ibaraki, Osaka 567-0047 Japan

Monday PM — Room: 3016
February 14, 2005 — Location: Moscone West Convention Center

Session Chairs: Sinn-Wen Chen, National Tsing-Hua University, Dept. of Cheml. Engrg., Hsin-chu 300 Taiwan; Srinivas Chada, Jabil Circuit Inc., FAR Lab/Advd. Mfg. Tech., St. Petersburg, FL 33716 USA

2:00 PM Invited
Thermal Stability Enhancement in Sputtered Cu Films Containing Insoluble Tungsten Carbides: *Yung-Yen Hsieh*[1]; Jinn Chu[1]; C. H. Lin[1]; T. Mahalingam[2]; [1]National Taiwan Ocean University, Inst. of Matls. Engrg., Keelung Taiwan; [2]Alagappa University, Dept. of Physics India

In this paper, we report enhanced thermal stabilities of nanostructured Cu films containing insoluble tungsten carbides prepared by sputtering. Tungsten carbides in the form of W_2C are present in the supersaturated solid solution of Cu, as confirmed by X-ray photoelectron spectroscopy and X-ray diffraction. Focused ion beam analysis reveals that the films are thermally stable during annealing when they are in contact with Si and the copper silicide is not formed up to an annealing temperature 530°C. The films exhibit good thermal stability at high temperatures and it can be rationalized as a consequence of a refined grain structure together with the strengthening effect of W_2C.

2:30 PM
Thermal Stability Improvement Study of Sputtered Cu Films with Insoluble Substances: *Chon-Hsin Lin*[1]; Jinn Chu[1]; Yung-Yen Hsieh[1]; T. Mahalingam[2]; *Chun-Hui Lin*[1]; S.F. Wang[3]; [1]National Taiwan Ocean University, Inst. of Matl. Engrg., Keelung Taiwan; [2]Alagappa University, Physics, India; [3]National Taipei University of Technology, Depts. of Matls. & Minerals Resources Engrg.

Copper is an attractive material for metallization in microelectronics, because of its low resistivity and high reliability against electromigration compared with Al and its alloys. However, Cu diffuses readily into Si and SiO_2, resulting in the formation of copper silicide compounds at low temperatures. Our prior studies confirmed the better thermal stability of Cu-W and Cu-Mo and showed that a low film resistivity could be achieved by adding small amounts of insoluble elements with the fine-grained film microstructure after annealing. In present study, dilute amounts of insoluble substances were introduced in Cu film during sputtering. A newly developed Cu metallization process is proposed with a self-forming barrier between Cu film and Si by vacuum thermal annealing. The process can improve the thermal stability of Cu and suppress Cu diffusion into the Si substrates, retaining a low resistivity of Cu. The thermal stability of Cu film produced by this process was characterized by various techniques such as X-ray diffraction, focus ion beam (FIB), secondary ion mass spectroscopy (SIMS), transmission electron microscope (TEM), X-ray photoelec-

tron spectroscopy (XPS), electrical resistivity and current-voltage (I-V) curve measurements, and the results are discussed.

2:50 PM
Crystallization and Failure Behaviors of Ta-TM (TM=Fe, Co) Nanostructured/Amorphous Diffusion Barriers for Copper Metallization: *Jau Shiung Fang*[1]; C. P. Hsu[2]; G. S. Chen[3]; [1]National Huwei University of Science and Technology, Dept. of Matls. Sci. & Engrg., 64 Wunhua Rd., Huiwei, Yunlin 632 Taiwan; [2]National Huwei University of Science and Technology, Grad. Inst. of Electro-Optical & Matl. Sci., 64 Wunhua Rd., Huiwei, Yunlin 632 Taiwan; [3]Feng Chia University, Dept. of Matl. Sci., Taichung 410 Taiwan

This work examines the thin-film properties and diffusion barrier behaviors of sputtered Ta-TM (TM=Fe, Co) films, aiming at depositing a highly crystallization-resistant and conductive diffusion barriers for Cu metallization. Four-point probe measurements, X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were used to examine the barrier properties. Structural examination indicted that intermetallic-compound-free amorphous Ta-TM films were obtained by magnetron sputtering, and thus giving a resistivity about 146.82 ìÙ-cm .and 247.01ìÙ-cm for Ta50Fe50 and Ta50Co50 films, respectively. The Si/Ta50Fe50/Cu and Si/Ta50Co50/Cu stacked samples were observed to fail completely at temperature above 600°C and 650°C because of the formation of Cu3Si protrusions between silicon and Ta-TM barrier layer. Highly thermal stabilized amorphous Ta-TM thin film can thus be potentially adopted as a diffusion barrier for Cu metallization.

3:10 PM
Interfacial Reactions in the Al/Ta Couples: *Chin-Yi Chou*[2]; Sinn-Wen Chen[1]; [1]National Tsing-Hua University, Chem. Engrg. Dept., #101, Sec. 2, Kuang-Fu Rd., Hsin-Chu 300 Taiwan; [2]National Tsing-Hua University, Matls. Sci. & Engrg. Dept., Hsin-Chu 300 Taiwan

Thermal inkjet technology is in widespread use for color printers, and the market is still growing. Tantalum has low contact resistance, good adhesion and chemical resistance and is used as the diffusion barrier between the gold and aluminum layers. Understanding of the Al/Ta contact stability is fundamentally important for the inkjet technology. This study investigated the Al/Ta contact stability using the reaction couple technique. A Ta foil and an Al chunk were polished, placed together in a graphite mold, and sealed in a quartz tube under vacuum. The quartz capsule was annealed in a furnace at 750 and 900°C for various lengths of time. After heat treatment, the couple was examined metallographically using SEM and optical microscopy. Reaction layers were formed at the interfaces. The composition of the reaction layer was determined using EDS, and a compositional homogeneity range was observed for the Al3Ta phase.

3:30 PM
Solid State Reaction in the Au-Cu Wire Connection with Al-Cu Pad During Aging: *Guh-Yaw Jang*[1]; Jenq-Gong Duh[1]; Hideyuki Takahashi[2]; David Su[3]; [1]National Tsing Hua University, Dept. of Matls. Sci. & Engrg., 101 Sec. 2 Kuang-Fu Rd., Hsinchu 300 Taiwan; [2]JEOL Ltd., Application & Rsch. Ctr., Tokyo Japan; [3]TSMC Ltd., Failure Analy. Div., 9, Creation Rd., 1, Sci.-Based Industl. Park, Hsinchu 300 Taiwan

In integrated-circuit packages, wire bonding technique is the preferred method for making electrical connections between the chip and lead frame. The influence of aging at 150°C from 0 h to 3000 h for interfacial reaction of the Au-Cu wire bonded with Al-Cu pad was investigated in this study. The wire-bond were first cold mounted in epoxy and then sectioned by using a slow speed diamond saw. Cross-sectional samples were ground and polished. To observe various intermetallic compounds (IMCs) and fine voids with field-emission scanning electron microscope, polished samples were ion milled with precision etching and coating system. The $Au_5(Al,Cu)_2$ IMC was found between Au-Cu wire and Al-Cu pad in the as-assembled wire-bond. After aging for 168 h, $Au_2(Al,Cu)$ IMC formed in the edge of wire-bond. The Al-Cu pad was consumed completely after aging for 500 h, and $Au_4(Al,Cu)$ IMC was observed at the Au-Cu wire/$Au_5(Al,Cu)_2$ interface. It was revealed that $Au_5(Al,Cu)_2$ IMC would be entirely transformed into $Au_4(Al,Cu)$ IMC in the wire-bond aged more than 1000 h. With the aid of microstructure evolution, quantitative analysis, the interfacial phase transformation between Au-Cu wire and Al-Cu pad could be probed and revealed.

3:50 PM Break

4:10 PM
Thermomigration of SnPb Solder Bump and Effect on Coarsening of Microstructure: *Y. C. Chuang*[1]; *Cheng-Yi Liu*[1]; [1]National Central University, Chemi. & Matls. Engrg., No.300, Jungda Rd., Jhongli, Taoyuan 320 Taiwan

Thermomigration(TM) is the net atomic flux driven by a thermal gradient. It has been reported that the TM-induced atomic transportation could be a serious reliability issue in C4 solder bump. Therefore, the study of solder thermomigration deserves a serious attention. In this study, stable thermal gradient (1000°/cm) has been created along a SnPb solder joint. The TM atomic flux was determined to be J=9.96 atom/cm2.s and we also obtain the important TM parameter, molar heat flux, Q??= 0.904 kJ/mole. Coarsening in SnPb solder has been studied by numerous researchers. Interestingly, we found that TM will affect coarsening behavior of SnPb solder bump. The detail kinetics of coarsening in the microstructure of SnPb solder under the effect of TM will be presented in this talk.

4:30 PM
Electromigration Effects at Bimetallic Interfaces: *Helen Theresa Orchard*[1]; Lindsay Greer[1]; [1]University of Cambridge, Matls. Sci. & Metall., Pembroke St., Cambridge CB2 3QZ UK

Electromigration is important to consider in integrated-circuit design as current densities in interconnects can approach 10^10 A m-2. At bimetallic interfaces, however, even lower current densities can strongly affect the growth of intermetallic compounds. Such diffusion and intermetallic compound formation are relevant, for example, for the reliability of wire bonds and vias on integrated circuits, and continue to be studied as operating conditions, including temperature, become more extreme. Existing analyses of electromigration at bimetallic interfaces are for cases in which compound growth is diffusion-controlled. For thin films, however, interfacial reaction barriers can be important and even dominate over diffusion control [Gösele and Tu, J. Appl. Phys. 53 (1982) 3252]. In the current paper, earlier analyses of electromigration effects are extended to include both diffusion and reaction kinetics. Wire bonds for high-temperature electronics are used as a case study, with interpretation of microstructural observations and discussion of further implications.

4:50 PM
Electric Current Effects on Metal-Metal Reactions: *Javier E. Garay*[1]; Umberto Anselmi-Tamburini[2]; Zuhair A. Munir[2]; [1]University of California, Dept. of Mechl. Engrg., Bourns Hall, Riverside, CA 92521 USA; [2]University of California, Chemi. Engrg. & Matls. Sci., Davis, CA USA

The effect of high-density direct current upon metallic systems was studied with the aim of decoupling Joule heat effects from other intrinsic effect. Investigations on interfacial reactions in the Ni-Ti and Cu-Ni system were carried out. Current densities of up to 2546 A.cm-2 were used in the temperature range of 625-850ºC. All of the intermetallic compounds (NiTi, Ni3Ti and NiTi2) present in the equilibrium phase diagram were identified in the product layer. In addition, b-Ti solid solutions formed in samples annealed above the a ® b temperature, 765ºC. The growth of all product layers was found to be parabolic and the applied current was found to significantly increase the growth rate of the intermetallic layers. In the Cu-Ni system, the effct of DC current was directional as the current was found to increase the diffusivity of Ni atoms in the direction that electrons were traveling in. The results on currents are explained in terms of current induced changes in the growth mechanism arising from changes in point defect mobility.

5:10 PM
Copper Hole Filling by Pulse Reverse Electroplating Method in 3-D SIP: Jin-Soo Bae[1]; Gun-Ho Jang[1]; *Jae-Ho Lee*[1]; [1]Hongik University, Matls. Sci. & Engrg., 72-1 Sangsu-dong, Mapo-gu, Seoul 121-791 USA

Copper hole filling is the important factor in 3-D stacking interconnection of SIP(system in package). As the packing density is getting higher, the hole size is getting smaller. When DC electroplating is applied, defect-free hole cannot be obtained in small size hole. To prevent the defects in holes, pulse and pulse reverse current was appiled in copper hole filling. The size of holes are 50, 75, 100 micron in diameter and 100 micron in height. The holes were prepared by DRIE method. TaN and Ta was sputtered for copper diffusion barrier. Hole specimen were filled by DC, pulse and pulse/reverse current electroplating methods. The effects of current types on copper deposits were investigated. Cross section of holes were observed by SEM to find the defects in holes. When pulse reverse plating method was used, successful hole filling was obtained.

Phase Transformations Within Small-Size Systems: Order-Disorder Transformations

Sponsored by: Materials Processing & Manufacturing Division, MPMD-Phase Transformation Committee-(Jt. ASM-MSCTS), EMPMD/SMD-Chemistry & Physics of Materials Committee, EMPMD-Nanomaterials Committee

Program Organizers: Vijay K. Vasudevan, University of Cincinnati, Department of Chemical and Materials Engineering, Cincinnati, OH 45221-0012 USA; Robert D. Shull, National Institute of Standards and Testing, Metallurgy Division, Gaithersburg, MD 20899-8552 USA; George Spanos, Naval Research Laboratory, Physical Metallurgy Branch, Washington, DC 20375-5000 USA; Xinghang Zhang, Texas A&M University, Department of Mechanical Engineering, College Station, TX 77843-3123 USA

Monday PM Room: 3002
February 14, 2005 Location: Moscone West Convention Center

Session Chairs: Zhong-Lin Wang, Georgia Institute of Technology, Matls. Sci. & Engrg., Atlanta, GA 30332-0245 USA; David E. Laughlin, Carnegie Mellon University, Matls. Sci. & Engrg., Pittsburgh, PA 15213 USA

2:00 PM Invited
Phase Equilibria in Nanocrystalline Magnetic Recording Materials: *David E. Laughlin*[1]; Mihaela Tanase[2]; Yingguo Peng[1]; [1]Carnegie Mellon University, Matls. Sci. & Engrg., 5000 Forbes Ave., Pittsburgh, PA 15213 USA; [2]Carnegie Mellon University, Physics, 5000 Forbes Ave, Pittsburgh, PA 15213 USA

It is well known that the size of grains or particles plays an important role in their thermodynamics and hence phase equilibria. For example, small particles are known to have different transition temperatures than their bulk counterparts. In this paper we will look at the phase equilibrium that exists in two important materials that are currently of interest as magnetic recording media, namely thin film Co based hcp alloys and nanoparticles of FePt. The role of the size of grains or particles on surface segregation will be discussed. For the case of FePt nanoparticles the role of particle size on the atomic ordering transition will be presented. Atomic ordering in particles may proceed either heterogeneously or homogeneously. Both these cases will be discussed. This research has been sponsored by the DSSC of CMU and SEAGATE Research of Pittsburgh, PA.

2:35 PM
The A1-L10 Phase Transition in the Alloy Nanoparticle: *Bo Yang*[1]; Mark D. Asta[1]; O. N. Mryasov[2]; T. Klemmer[2]; R. Chantrell[2]; [1]Northwestern University, Dept. of Matls. Sci. & Engrg., 2220 Campus Dr., Evanston, IL 60201 USA; [2]Seagate Research, 1251 Waterfront Place, Pittsburgh, PA 15222 USA

Monte-Carlo simulations are applied to investigate ordering processes in L10 alloy nanoparticles. We employ parametric, model-system studies to examine effects on nanoparticle ordering associated with reduced coordination and interfacial segregation, factors that become increasingly relevant as the surface to volume ratio increases with decreasing particle size. We also explore the kinetic pathways for nanoparticle ordering under the isothermal annealing conditions. On the basis of calculated long-range-order parameters defined to characterize chemical order in the context of magnetic properties, we find reduction in the thermodynamic ordering temperatures with decreasing nanoparticle size. This reduction of the ordering temperatures is found to be enhanced with an increasing driving force for the surface/interface segregation. We find a tendency toward the formation of the metastable multidomain configurations under the condition of isothermal annealing from disordered fcc nanoparticles state.

3:00 PM
Size Dependence of $L1_0$ Ordering in FePt Nanoparticles: Y. K. Takahashi[1]; T. Koyama[1]; T. Ohkubo[1]; *K. Hono*[1]; [1]National Institute for Materials Science, 1-2-1 Sengen, Tsukuba 305-0047 Japan

As the recording density approached to 1 Tbit/in2, the size of recording bit will be smaller than 10 nm. To overcome the thermal instability due to the reduction of the size, L10-FePt with a large magnetocrystalline anisotropy is thought to be the most promising material for ultrahigh density magnetic recording media appliations. Since as sputtered films have disordered fcc strcutrue, they must be ordered to the L10 structure either by in-situ annealing or post annealing. In the course of the studies of ordering from fcc to L10 FePt, we found that there is a size dependence of the ordering when the particle size become smaller than approximately 5 nm. Simple Bragg-Williams calculation supports that the ordering becomes unstable when the particle size become smaller than a critical size. The critical size depends on the interfacial energy. This finding indicates that we must consider both the superparamagnetic limit and the ordering limit when we design the FePt recording media.

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3:40 PM Invited
Structure, Phase Transformation and Twinning of Magnetic Nanocrystals: *Zhong Lin Wang*[1]; [1]Georgia Institute of Technology, Sch. of Matls. Sci. & Engrg., 771 Ferst Dr., NW, Rm. 163, Love Mfg. Bldg., Atlanta, GA 30332-0245 USA

Depending on the Fe to Pt elemental ratio, the Fe-Pt alloys can display chemically disordered face centered cubic phase or chemically ordered phases. We report detailed microscopic studies on phase transformation, coalescence and twin structure formation of thermally annealed 6 nm FePt nanocrystals under high vacuum on an amorphous carbon surface. Our high-resolution transmission electron microscopy (HRTEM) studies show that A1 to $L1_0$ phase transformation occurs at 530°C. The multilayered nanocrystal assemblies coalesce to form larger grains at 600°C. Shape and surface atomic arrangement of the monodisperse FePt magnetic nanocrystals and their evolution induced by annealing have been studied. Truncated octahedron enclosed by flat {100}, stepped {111} and zig-zag {110} facets is the dominant shape adopted by the as-synthesized FePt nanocrystals. The Marks decahedron shaped FePt nanocrystals and icosahedron related multiply twined FePt nanocrystals are also identified in the as-synthesized nanocrystals. A new structural model the multiply twined nanocrystals related to icosahedron has been proposed. After annealing, the {110} facet disappears; the regular cuboctahedron becomes a dominant shape for the chemically ordered FePt nanocrystals. Atomic arrangement on the FePt nanocrystals surfaces is the same as that in the volume although some defects such as atomic steps and kinks exist. Iron atoms are preferably the terminating layer of the {100} surface after annealing. Thanks to the contribution made by Drs. S.H. Sun, H. Zeng, J.P. Liu, J. Li and Z.R. Dai.

4:15 PM
Ordering Reaction and Sintering Behavior in [FePt]100-xCrx Nanoparticles: *Chandan Srivastava*[1]; Gregory B. Thompson[1]; James W. Harrell[2]; David E. Nikles[3]; [1]University of Alabama, Metallurgl. & Matls. Engrg., Box 870202, Tuscaloosa, AL 34587 USA; [2]University of Alabama, Dept. of Physics, 206 Gallalee Hall, Box 870324, Tuscaloosa, AL 35487 USA; [3]University of Alabama, Dept. of Chmst., Box 870336, Tuscaloosa, AL 35487-0336 USA

We report the effect of incorporating Cr into FePt nanoparticles as a mechanism to reduce the ordering temperature while magnetically decoupling sintered nanoparticles. Self-assembled arrays of FePt nanoparticles are potential systems for next-generation magnetic recording. STEM/EDX measurements and XRD confirmed that Cr was successfully incorporated into the FePt lattice in the as-synthesized state. Upon increasing the temperature, the Cr does not precipitate out of the particle, even after L10 ordering. XRD indicates a modest increase of the lattice spacing of the [FePt]100-xCrx at temperatures prior to the L10 phase transformation. This lattice expansion behavior is not observed in FePt nanoparticles. Scherrer analysis of the XRD peak widths indicate that Cr hinders grain growth in the sintered particles at elevated temperatures. A series of time and temperature coercivity measurements for the [FePt]100-xCrx will be presented and discussed in terms of the phase transformation and sintered morphology of the nanoparticles.

Shape Casting — The John Campbell Symposium: Filling and Feeding

Sponsored by: Light Metals Division, LMD-Aluminum Committee, MPMD-Solidification Committee
Program Organizers: Murat Tiryakioglu, Robert Morris University, Moon Township, PA 15108 USA; Paul N. Crepeau, General Motors Corporation, MC/486-710-251, Pontiac, MI 48340-2920 USA

Monday PM Room: 2008
February 14, 2005 Location: Moscone West Convention Center

Session Chair: John T. Berry, Mississippi State University, Mississippi State, MS 39762-5925 USA

2:00 PM
Gating Design After Campbell - A Practical Experience of the Daily Struggle With Porosity: *Salvador Valtierra*[1]; [1]Nemak, R&D, Arco Vial Km 3.8, Garcia, Nuevo Leon 66000 Mexico

Gating design can be considered as an Art, Religion, Science or sorcery (actually we are not sure about any of them at all!) In the 60s (Ancient history BC) gating considered mainly the effect of shape and size of gating systems on the speed of flow. And some deviations to the hydraulic model to refine the systems, introducing heat losses into the gating systems. Despite the huge amount of information coupled with computer simulation the successful design of a casting system was not always achievable. History can be rewritten after Campbell contributions. The present work shares the experience accumulated during 12 years of a love-hate relationship with oxides generated by bad gating designs. Also a description of the resulting collection of oxides, bubbles trails and accompanying friends, observed in castings poured in semi-permanent molds using traditional gating designs. These are compared with the successful results obtained when using Campbell's rules.

2:25 PM
Filling Mold Cavities at High Flow Velocities Without Turbulence: *John L. Jorstad*[1]; Mike Thieman[2]; [1]JLJ Technologies, Inc., 9112 Donora Dr., Richmond, VA 23229 USA; [2]THT Presses, Inc., 7475 Webster St., Dayton, OH 45414 USA

Professor Campbell has long taught that molten aluminum that exceeds 0.5 meters/second flow velocity during casting is increasingly prone to turbulence-related defects such as oxide folds that significantly reduce component performance. Semi solid aluminum melts behave quite differently. Partially solidified melts having a significant fractions of solid (approximately 50%) can flow at velocities exceeding 2 meters/second while still maintaining a stable flow front. The viscosity of molten aluminum increases as the fraction solid becomes greater, and the more viscous a melt, the faster it can flow without turbulence. Semi solid melts are thus better-able than liquid to fill thin and very detailed mold cavities while still producing high integrity parts. This paper will describe the results of set of casting trials wherein the effects of in-gate velocity on casting integrity was determined while casting liquid as well as semi solid A356 alloy.

2:50 PM
Designing Reliable Castings: *Malcolm Blair*[1]; Raymond W. Monroe[1]; Christoph Beckermann[2]; Richard Hardin[2]; Kent Carlson[2]; John Griffin[3]; Charles Monroe[2]; [1]Steel Founders' Society of America, 780 McArdle Dr., Unit G, Crystal Lake, IL 60014 USA; [2]University of Iowa, Mechl. Engrg., 2212 Engrg. Bldg., Iowa City, IA 52242-1527 USA; [3]University of Alabama, Matls. Sci. & Engrg., 1016 15th St. S., Birmingham, AL 35294-4552 USA

Castings offer flexible and efficient design solutions for many products. However, designs are generally based on strengths of materials calculations and the experience of the designer. Industrial experience with current products tends to dominate in the development of future designs. This process leads to an incremental development of design utilizing factors of safety, which lead to increasing weights of components and inevitably inefficient uses of materials. Factors of safety are a way of developing cushions to avoid the unforeseen failures because of unexpected loads on the part or reductions in expected properties due to their manufacture. All product forms are subject to this paradigm. In castings the unquantifiable factors such as shrinkage, microshrinkage and surface indications lead to more and more conservative design rules. Non-destructive testing such as radiography and surface inspection do not give the designer any way of assessing the effect of shrinkage or surface indications. Programs to design for these casting features and develop new non-destructive standards and techniques are essential to the efficient use of castings. Work to develop more quantitative design rules are addressing the issue of shrinkage and surface indications. The development of new quantitative design rules for castings is progressing for steel castings through an integrated approach between producers, users and researchers.

3:15 PM
Vortex-Gate Design for Gravity Casting: *Fu-Yuan Hsu*[1]; Mark R. Jolly[2]; John Campbell[2]; [1]Auspicium Co., Ltd., 2F-3, No. 4, Sec. 1, Jen-Ai Rd., Taipei Taiwan; [2]University of Birmingham, IRC in Matls. for High Performance Applications, Edgbaston, Birmingham B15 2TT UK

A novel runner system design, named a Vortex-Gate, has been explored for aluminum gravity casting. Using this design the velocity of flow of the liquid metal flow was controlled below the critical value and, at the same time, a high flow rate was maintained and the flow behavior does not appear to generate "bi-film" defects. The "virtual" experiment using a computational modeling package, and the "physical" experiment, a real-time X-ray radiography study, were found to be in reasonable agreement.

3:40 PM Break

3:50 PM
Characterization of Metal Filling Behavior of Lost Foam Castings Using Real Time X-Ray Technology: *Wanliang Sun*[1]; Harry E. Littleton[1]; Charles E. Bates[1]; [1]University of Alabama, Matls. Sci. & Engrg., 917 Bldg., 1530 3rd Ave. S., Birmingham, AL 35294-4480 USA

Characterization of metal filling behavior of lost foam castings is very important to understand, and in turn control the foam pyrolysis products related casting defects. In this study, metal filling of lost foam castings at various conditions was characterized using non-invasive real time X-Ray visualizations. A simple rectangular plate was used as casting sample. Parameters such as metal filling velocity, number of metal converging lines, metal front profile and metal progressing angle were used to characterize the metal filling behavior. Metal filling behaviors under different process variables such as foam pattern fusion level, coating permeability, casting thickness, glue joint types and gating types were investigated. It is observed that under different conditions, the metal filling of lost foam castings changed significantly. Correlation between process parameters and metal filling behavior will assist the process control of the lost foam casting process.

4:10 PM
The Five Feeding Mechanisms: *Christopher Malcolm Gourlay*[1]; Arne Kristian Dahle[1]; [1]University of Queensland, CRC for Cast Metals Mfg. (CAST), Sch. of Engrg., St. Lucia, Queensland 4072 Australia

This paper summarises a number of studies on the rheology of solidifying alloys and discusses these results with reference to the five feeding mechanisms proposed by Campbell. Distinct changes in rheological response at the coherency and maximum packing solid fractions are correlated with transitions between feeding mechanisms. The effect of alloy and solidification conditions on the development of mush strength during solidification is discussed with respect to the operating feeding mechanisms and particular attention is given to the role of burst feeding. A similar mechanism is also shown to operate in the formation of banded defects. The distribution of solid within a casting can affect where different feeding mechanisms operate. Results are presented showing that when filling occurs with partially solid material, the crystals migrate towards the centre of the cross-section. This leads to uneven solid fraction distributions in the cavity and therefore local areas of lower solid fraction which can operate as preferential feeding paths.

4:30 PM
Experimental Quantification of Interdendritic Permeability: *Øyvind Nielsen*[1]; Svein Ove Olsen[1]; [1]SINTEF, Matls. & Chmst., PB 124 Blindern, Oslo 0314 Norway

The interdendritic permeability is a key parameter for the understanding of feedability and porosity formation in shaped castings. In the present work, a permeameter has been developed in which a melt is cast into a vertical steel pipe encompassed by two independent tube furnaces (top and bottom), used to set up a thermal gradient that promotes directional solidification from the bottom. The sample temperature is measured by a series of thermocouples along the sample length, and the pipe bottom is opened when the temperature close to the bottom reaches a predefined value in the solidification interval. Thus, interdendritic liquid is allowed to exude through the bottom sample surface, and the flow rate is measured with a graphite float placed at the top surface. The advantages with the design are: (i) the special flux alloys used in previous permeameters are not needed because the top surface remains liquid throughout the experiment, (ii)

the cooling rate can be controlled, and (iii) the temperature at which interdendritic feeding stops can be measured. Experiments have been carried out for A356, and the measured interdendritic flow rates have been used to quantify the differences in feedability due to the addition of grain refiner and modification by strontium. The results can be used e.g., to shed light on the well-known increase in microporosity with increasing strontium content. The main challenge with the experiment is the fact that the solid fraction, and thus the permeability, varies along the sample length. A mathematical model, taking into account the macrosegregation formation due to shrinkage and exudation, that can be used to extract permeability data from the measurements is being developed.

4:50 PM
The Critical Gate Velocities for Magnesium Casting Alloys (ZK51A): *Farhad Bahreinian*[1]; [1]University of Toronto, Matls. & Sci. Engrg., 184 College St., Rm. #140, C/O Prof. S. Argyropulos, Toronto, Ontario M5S 3E4 Canada

The effects of gate entry velocity on the soundness of the ZK51A Alloy were investigated by considering a new theory, The Critical Gate Velocities. The surface turbulence and oxide layer formation were evaluated using an accurate video camera. The results show that in this alloy, the critical gate velocity is about 0.5 m/s. Surface turbulence phenomenon occurs at velocities more than 0.5 m/s, which decreases the mechanical properties. The critical gate velocity decreases to 0.25 m/s when the casting thickness is 10 mm. The results are well correlated to the critical gate velocities values observed in aluminum alloys.

5:10 PM
The Connection Between Filling, Feeding and Applied Pressure in Cast Aluminum Alloys: *Rogelio Luck*[1]; Robert P. Taylor[1]; John T. Berry[1]; [1]Mississippi State University, Dept. of Mechl. Engrg., PO Box ME, Mississippi State, MS 39762 USA

Oxide bifilms often appear to be linked with the dispersed type of porosity observed in longer freezing range aluminum alloys. Although measures exist to help prevent the inadvertent incorporation and the subsequent unfurling of these bifilms into potential pores, little information would seem to be available specific to feeder design for this class of alloys. This is in contrast to the information available concerning the design of feeding systems for short freezing range alloys, in particular low-carbon steels, where macroscale shrinkage is liable to occur. The various measures required regarding solidification order, required feeder volume, range of feeding are plentiful for this second class of alloys and are more than adequately covered by Campbell's feeding rules. The paper attempts to draw together facts which might help fully quantify the needed guidelines for feeding long freezing range aluminum alloys.

Superalloys and Coatings for High Temperature Applications: Bond-Coat Technologies - II

Sponsored by: Structural Materials Division, SMD-High Temperature Alloys Committee, SMD-Corrosion and Environmental Effects Committee-(Jt. ASM-MSCTS), High Temperature Materials Committee of IoM3
Program Organizers: Roger C. Reed, University of British Columbia, Department of Metals and Materials Engineering, Vancouver, British Columbia V6T 1Z4 Canada; Richard S. Bellows, Solar Turbines, Inc., Materials and Process Engineering, San Diego, CA 92186-5376 USA; Qiang (Charles) Feng, University of Michigan, Department of Materials Science and Engineering, Ann Arbor, MI 48109 USA; Tim Gabb, NASA Glenn Research Center, Cleveland, OH 44135 USA; John Nicholls, Cranfield University, Bedfordshire MK43 OAL UK; Bruce A. Pint, Oak Ridge National Laboratory, Oak Ridge, TN 37831 USA

Monday PM — Room: Nob Hill A/B
February 14, 2005 — Location: San Francisco Marriott

Session Chairs: Richard S. Bellows, Solar Turbines Inc., Matls. & Process Engrg., San Diego, CA 92186-5376 USA; Qiang (Charles) Feng, University of Michigan, Dept. of Matls. Sci. & Engrg., Ann Arbor, MI 48109 USA

2:00 PM Invited
Integrated Approach to Superalloy and Coatings Technology Development: *David A. Litton*[1]; [1]Pratt & Whitney, Matls. & Processes Engrg., M/S 114-41, 400 Main St., E. Hartford, CT 06108 USA

To provide customers with higher performance and reduced operating costs, noise, and emissions, hot section engine component designs demand materials systems that can perform predictably in more hostile environments for longer exposures. To reduce maintenance costs, materials technologies that allow for refurbishment to extend service lives of parts over multiple engine overhauls are critical. For the same reasons, part count reduction is driving the design of parts with multiple airfoils such as integrally-bladed rotors and vane clusters. Integrated designs to monitor the condition of hot section components are under study to maximize uninterrupted service. These considerations multiply the constraints on the development of superalloy and coating materials and processing technology. This paper will correlate requirements for materials properties to these design constraints and summarize current approaches in materials and processing technology research and development to maximize customer value.

2:30 PM Invited
Secondary Reaction Zones in Coated Single Crystal Superalloys: *Pierre Caron*[1]; Odile Lavigne[1]; Catherine Ramusat[1]; [1]ONERA, DMMP/MHT, 29, Ave. de la Div. Leclerc, Châtillon 92322 France

In addition to the usual interdiffusion zone existing between nickel-based superalloys and their overlay or aluminide protective coatings, some secondary reaction zones (SRZ) may form on certain conditions. SRZ have a deleterious effect on the mechanical strength of the alloy substrate when extending over several tens of micrometers. Occurrence of SRZ beneath a Pt-modified aluminide bond coat has been checked in a number of superalloys in order to determine the influence of the substrate chemistry. More specifically, minor and major compositional modifications as well as stress relaxing heat treatments have been tested in a new generation Re and Ru bearing single crystal superalloy in order to avoid the formation of SRZ. The microstructure of the specimens has been investigated in the as-coated state and after long-term high temperature ageing treatments.

3:00 PM
The Effect of Alloy Composition on the Precipitation of Topological Close Packed Phases at Aluminide Coatings on Superalloys: *Catherine Mary Rae*[1]; Matthew Simon Hook[1]; Roger C. Reed[2]; [1]Cambridge University, Dept. of Matls. Sci., Pembroke St., Cambridge CB2 3QZ UK; [2]University of British Columbia, Dept. of Metals & Matls. Engrg., 309-6350 Stores Rd., Vancouver, BC V6T 1Z4 Canada

Aluminide coatings provide considerable protection for turbine components subjected to hostile environments. However, inter-diffusion between the coating and the substrate causes changes in the phase composition and morphology which destroys the creep resistance of the alloy in the affected area and which, in a thin walled section, can considerably reduce the ability of the component to support load. We have compared the evolution of low temperature, high activity Aluminide and Platinum-modified Aluminide coatings on three very different alloys; RR3000, CMSX-4 and TMS75. We discuss the factors determining the distribution of the refractory elements in these coatings we observe that the precipitation of TCP phases in the interdiffusion zone varies considerably with the alloy composition. The morphology determines the speed with which the precipitates form, and we suggest that this may control the rate of ingress of the coating into the substrate and also the formation of the secondary reaction zone.

3:25 PM
Microstructure and Mechanical Properties of Al-Ni-Ru Alloys: *Fang Cao*[1]; Qiang Feng[1]; Tresa M. Pollock[1]; [1]University of Michigan, 3062 H. H. Dow Bld., 2300 Hayward St., Ann Arbor, MI 48109 USA

Systems based on RuAl have the potential to perform as bond coat materials in superalloy-Thermal Barrier Coating (TBC) systems for advanced gas turbine engines. For coating applications, an understanding of the ternary Ni-Al-Ru system is essential since diffusion of Ni from the Ni-based superalloy substrate is unavoidable during manufacture and service of the TBC systems. In order to address this subject, alloys with selected compositions in the Al-Ni-Ru system were melted by Crystalox induction cold crucible melting and the microstructure and present phases were examined. Compression tests were performed at room temperature up to 973 K for these alloys. Creep behavior was investigated by compression creep tests at 1273K in vacuum condition. Finally, the deformation mechanism was studied by dislocation substructure analysis and identification.

3:50 PM Break

4:10 PM Invited
Cost Reductions in the Aerospace Coatings Industry: *Ken S. Murphy*[1]; [1]Howmet Research Center, 1500 S. Warner St., Whitehall, MI 49461 USA

Cost reductions come from many places in the manufacturing process. Some are from the systems used, the empowerment of workers to effect change, and relationships with suppliers in addition to the traditional process/equipment improvements and raw material costs. This paper describes how the various management techniques and alternative material selection are integrated into the aerospace coating shop floor. It will discuss how the Alcoa Business System has impacted cost at Howmet - Thermatech Coatings and how Palladium is being assessed as an alternative to Platinum as the noble metal used in high temperature diffusion aluminide coatings.

4:40 PM
Superalloy-Dependent Stability of β-NiAl Phase in MCrAlY Coatings: *Emmanuel Perez*[1]; Travis Patterson[1]; Yong-Ho Sohn[1]; [1]University of Central Florida, Advd. Matls. Procg. & Analy. Ctr. & Dept. of Mechl., Matls. & Aeros. Engrg., Orlando, FL 32816-2455 USA

Hot section components in gas turbines can be MCrAlY-coated to provide the component with an Al reservoir that maintains a protective oxide later on the coating's surface. Over the service life of the component, the coatings degrade by composition and phase changes due to oxidation/hot-corrosion on the coating's surface, and due to multicomponent interdiffusion from and into the superalloy substrate. This interdiffusion process leads to Al depletion from the coating, and in many cases is the life-limiting factor. In this study, the rate of degradation for MCrAlY coatings on several Ni-base superalloys was examined with an emphasis on the composition-dependence of Al interdiffusion. Several diffusion couples have been prepared to examine the composition-dependence of Al with several Ni-base superalloys. Concentration profiles obtained from EDS and EPMA were analyzed to determine the effective interdiffusion coefficient. These results will be discussed in terms of composition-dependence of the Al interdiffusion and the phase stability of β-NiAl in MCrAlY coatings.

5:05 PM
Inhomogeneous TGO Formation in Thermal Barrier Coatings with Rough Top-Coat/Bond-Coat Interfaces: *Feng Tang*[1]; Leonardo Ajdelsztajn[1]; Julie M. Schoenung[1]; [1]University of California, Cheml. Engrg. & Matls. Sci., One Shields Ave., Davis, CA 95616 USA

The thermal cycle lifetime of thermal barrier coatings (TBCs) is affected greatly by the features of the thermally grown oxides (TGOs). This paper presents our observation of inhomogeneous TGO formation as a result of the roughness profile at the top-coat/bond-coat interface. NiCrAlY bond coats were thermally sprayed with the LPPS and HVOF processes, and the YSZ top coats were sprayed with the APS process. These processes resulted in a rough bond coat/top coat interface. The TBC specimens were thermal cycled for more than 300 one-hour cycles, in air at 1121°C. It was found that the TGO that formed at the peaks in the roughness profile were notably thicker than the TGO that formed at other areas. The mechanisms for the inhomogeneous TGO formation and its effect on the TBC lifetime are discussed. Characterization methods included SEM, XRD, and EDS.

5:30 PM
The Development of the Virtual Coating Program: *Rudder Wu*[1]; Makoto Osawa[1]; Hiroshi Harada[1]; [1]National Institute for Materials Science, High Temp. Matls. Grp., 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047 Japan

A thermal barrier coating (TBC) simulation program based on the energy release rate model has been developed to evaluate delamination along the TGO/bond coat interface. The program accepts three input categories including engine parameters (overhaul/cruising TIT, thin-film cooling), aviation parameters (flight time/cycles, taking-off/thrust-reversal time) and material properties. Based on these parameters, real-time cyclic temperature profile across the thickness of a TBC system is generated. Consequently, the empirically-determined parabolic functions of top coat sintering and TGO growth were also ascertained in the calculation. Upon correlating the calculated energy release rate with the published mode II interface toughness ($50Jm^{-2} \leq \Gamma \leq 80Jm^{-2}$), a critical TGO thickness of ~ 3-4 microns depending on the extent of top coat sintering was obtained, comparable to that observed in a commercially used nozzle-guided vane. Therefore, this program serves as a platform for TBC design and enables lifetime prediction and lifetime-remaining assessments.

Surface Engineering in Materials Science - III: Laser Processing for Surface Modification

Sponsored by: Materials Processing and Manufacturing Division, MPMD-Surface Engineering Committee
Program Organizers: Arvind Agarwal, Florida International University, Department of Mechanical and Materials Engineering, Miami, FL 33174 USA; Craig Blue, Oak Ridge National Laboratory, Materials Processing Group, Metals and Ceramic Division, Oak Ridge, TN 37831 USA; Narendra B. Dahotre, University of Tennessee, Department of Materials Science & Engineering, Knoxville, TN 37932 USA; John J. Moore, Colorado School of Mines, Department of Metallurgy and Materials Engineering, Golden, CO 80401 USA; Sudipta Seal, University of Central Florida, Advanced Materials Processing and Analysis Center and Mechanical, Materials and Aerospace Engineering, Oviedo, FL 32765-7962 USA

Monday PM — Room: 2022
February 14, 2005 — Location: Moscone West Convention Center

Session Chairs: Narendra B. Dahotre, University of Tennessee, Dept. of Matl. Sci. & Engrg., Knoxville, TN 37932 USA; Roger Narayan, Georgia Tech, Sch. of Matls. Sci. & Engrg., Atlanta, GA 30332-0245 USA

2:00 PM
Laser Deposition of Titanium Boride Reinforced Titanium Alloy Composites: *Davion Hill*[1]; Rajarshi Banerjee[1]; Jaimie Tiley[2]; Peter C. Collins[1]; Hamish L. Fraser[1]; [1]Ohio State University, Matls. Sci. & Engrg., 477 Watts Hall, 2041 College Rd., Columbus, OH 43210 USA; [2]Air Force Research Laboratory, Matls. & Mfg. Direct., Dayton, OH USA

Due to their wide applicability, there is considerable interest in the development of metal-matrix composites consisting of hard precipitates, such as transition-metal borides, dispersed in a metallic/alloy matrix. One such system that has generated considerable interest in recent years is the titanium boride in titanium alloy matrix system. Laser engineered net-shaping (LENS™) is a directed laser deposition process which uses a powder feedstock and appears to be a promising technology for the processing of these metal-matrix composites. Two types of TiB reinforced composites have been studied, one with an a+b matrix based on the alloy Ti-6Al-4V and the other with a primarily b matrix based on the alloy Ti-5Al-5V-5Mo-3Cr-0.5Fe (TIMETAL 5553). Using a feedstock consisting of a blend of pre-alloyed Ti-6Al-4V (or TIMETAL 5553) and elemental boron powders, these composites have been deposited in a single step via the LENS™ process. These as-deposited composites exhibit a refined homogeneous distribution of TiB precipitates within the alloy matrix, a consequence of the rapid solidification rates inherent to the LENS™ process. The microstructure of the LENS™ deposited composites has been investigated in detail using SEM and TEM based techniques. The room temperature tensile properties and wear resistance of these composites is currently being investigated and will be presented in this paper.

2:20 PM
Laser Processing of Bulk Crystalline Alloys for Improved Corrosion Resistance: *J. G. Hoekstra*[1]; G. J. Shiflet[1]; S. J. Poon[2]; J. R. Scully[1]; J. M. Fitz-Gerald[1]; [1]University of Virginia, Dept. of Matls. Sci. & Engrg., Charlottesville, VA USA; [2]University of Virginia, Dept. of Physics, Charlottesville, VA USA

In general it has been shown that amorphous metals have several attractive properties, particularly in areas of wear and corrosion resistance. Advances in metallic glass chemistries with enhanced solidification characteristics have furthered the development of bulk metallic glasses. In this study laser surface treatments were conducted in two alloy systems with glass forming abilities: Al and Fe based alloys. Cross-sectional analysis showed melt depths ranging from 0.5 to 3 microns largely dependent on the total surface dose. The resulting microstructures were correlated with electrochemical analysis and devitrification behavior. Potentiodynamic polarization results and impedance measurements show significant improvement over native materials, exhibiting several characteristics of amorphous surface layers. Characterization was performed by electron microscopy (SEM), energy dispersion (EDS), diffraction (XRD), and electrochemical analysis.

2:40 PM
Pulsed Laser Deposition of Tetrahedral Amorphous Carbon Nanocomposites: *Roger Jagdish Narayan*[1]; [1]Georgia Institute of

Technology, Sch. of Matls. Sci. & Engrg., 771 Ferst Dr. NW, Rm. 361, Atlanta, GA 30332-0245 USA

Tetrahedral amorphous carbon-metal nanocomposite films of >1 micron thickness were deposited on Ti-Al-V alloy substrates using a novel multicomponent target design during pulsed laser deposition. We have created novel nanostructured tetrahedral amorphous carbon-silver and tetrahedral amorphous carbon-titanium nanocomposite thin films. These nanocomposite films were characterized using Z-contrast scanning transmission electron microscopy (STEM-Z) and electron energy loss spectroscopy (EELS). Scratch testing demonstrated good adhesion of tetrahedral amorphous carbon-metal nanocomposite films to Ti-Al-V alloy. Nanoindentation testing of the tetrahedral amorphous carbon-metal films demonstrated excellent hardness and modulus values, within the range of 35 GPa and 350 GPa, respectively. Wear testing demonstrated coating lifetimes in excess of 300,000 cycles for tests conducted in Ringer's USP solution under ~ 1 GPa initial maximum Hertzian pressure.

3:00 PM

Heat Absorbed by 410 Stainless Steel During Laser Surface Modification Processes: *Jaimin P. Rao*[1]; [1]Illinois Institute of Technology, 3001 S. Michigan Ave., Apt. # 1804, Chicago, IL 60616 USA

Energy absorption and temperature distribution within the substrate material plays a very important role in laser surface modification processes. This study is to investigate the amount of energy absorbed by 410 stainless steel, when it is irradiated by High Power Direct Diode laser. Both experimental and computational techniques are employed in this study. Power absorbed by the substrate is determined by using the measured temperature history in an inverse heat transfer analysis by FEM based HOTPOINT system. The spatial distribution of actual power intensity on the irradiated surface is obtained as a function of incident power level. The results show that the coefficient of net heat absorption is in the range of 50-70%, which agrees with the direct simulations and data available from literature. It is also found that power intensity distribution along long axis is not top hat as claimed by the manufacturer.

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Studies on Laser Composite Surfacing of Aluminium with Silicon Carbide and Alumina: *Jyotsna Dutta Majumdar*[1]; B. Ramesh Chandra[1]; A. K. Nath[2]; Indranil Manna[1]; [1]Indian Institute of Technology, Metallurgl. & Matls. Engrg., Kharagpur, W. Bengal 721302 India; [2]Centre for Advanced Technology, Laser R&D, Block B, Indore, Madhya Pradesh 452 013 India

The present study aims at improving the wear resistance of aluminium by forming a thin layer of SiC and Al2O3 dispersed metal matrix composite by laser surface engineering. Laser processing was carried out with a 2 kW continuous wave CO2 laser by pre-placing a thin layer of SiC and Al2O3 on the surface of Al substrate and subsequently melting the surface with high power laser. The main process variables for the present study were laser power, scan speed, particle chemistry and thickness of pre-placed layer. A detailed characterization of the modified zone was undertaken to study the the morphology and distribution of the particles. The average microhardness and wear resistance of the composite surfaced layer was studied in details to compare the influence of process parameters on the kinetics and mechanism of wear. Finally, the optimum processing zone for laser composite surfacing of Al with SiC and Al2O3 was derived.

3:40 PM Break

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Laser Cladding of W-Cu Composite on Bronze Substrate: *Sheng-Hui Wang*[1]; Lijue Xue[1]; [1]National Research Council of Canada, Integrated Mfg. Tech. Inst., 800 Collip Cir., London, ON N6G 4X8 Canada

The feasibility of depositing W-Cu composite overlays by laser cladding technique was explored. Two types of tungsten powders, with an average size of 10 microns and 32 microns, were used to deposit coatings with various thicknesses. It is shown that tungsten particles tend to separate from the copper molten pool or coalesce within it, which occurs more easily for the fine powders than for the coarse ones, making it simpler to deposit dense coatings with coarse tungsten powders. Laser cladding of uniform thick coatings was proven to be difficult, due to the separation of tungsten from copper. Nickel addition enhances the possibility of depositing uniform W-Cu composite coatings, preventing or limiting the segregation and separation of the constituents. The preliminary results indicate that, by adjusting processing parameters and powder-blend compositions, it is feasible to fabricate uniform W-Cu overlays with various thicknesses that are metallurgically bonded to the substrates.

4:15 PM

The Effects of Glass-Forming Coatings on Fatigue Behavior of 316L Stainless Steel: *Fengxiao Liu*[1]; W. Yuan[1]; C. L. Chiang[2]; J. P. Chu[2]; P. K. Liaw[1]; R. A. Buchanan[1]; [1]University of Tennessee, Dept. of Matls. Sci. & Engrg., Dougherty Engrg. Bldg., Knoxville, TN 37996 USA; [2]National Taiwan Ocean University, Inst. of Matls. Engrg., Keelung 202 Taiwan

The Zr-31Cu-13Al-9Ni (atomic percent) glass-forming coating was deposited onto the 316L stainless steel by magnetron sputtering, followed by subsequent annealing. The effects of the glass-forming coating on the fatigue behavior of the 316L stainless steel were investigated. The application of the coating gave rise to the significant increases in both the fatigue life and the fatigue limit. Depending on the stress applied to the steel, the fatigue life can be increased by 30 times, and the fatigue limit can be elevated by 30%. Compared with the annealed steel, the cold-rolled steel substrate increased the fatigue life due to the higher strength of the steel. The post heat treatment of the glass-forming coating lowered the fatigue life because of the partial crystallization of the coating. High compressive residual stresses introduced when depositing were determined by the curvature measurement. The fractography showed that the coating remained well adhered to the steel. The surface-roughness measurements also indicated the improvement of the surface conditions. Therefore, the improved fatigue behavior indicated that the excellent adherence of the coating to the steel, the improved surface condition, together with the high compressive residual stresses, were the main reasons for the improvement of the fatigue behavior of the coated steel system.

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Laser Melting of Graded Coatings (Fe-SiC-Ni-Cr) on AISI 316L Stainless Steel: *Dillibabu Sastikumar*[1]; Alagan Viswanathan[1]; M. Jamal Mohamed Jaffar[2]; A. K. Nath[3]; [1]National Institute of Technology, Dept. of Physics, Tiruchirappalli, Tamilnadu 620 015 India; [2]Jamal Mohamed College, Dept. of Physics, Tiruchirappalli, Tamilnadu 620 020 India; [3]Center for Advanced Technology, Industrial CO2 Laser Sec., Indore 452 013 India

AISI 316L Stainless steel is widely used in the aggressive corrosive environments because of its high corrosion resistance. However, its wear resistance is poor due to relatively low hardness (about 200 HV). It could not be hardened by heat treatment technique due to its austenitic phase. Different routes are being attempted using laser surface modification technique to improve its surface hardness. In this study, AISI 316L SS was preplaced with graded coatings of Fe-SiC-Ni-Cr and laser melted for improving its surface hardness. Three different compositions of Fe-SiC-Ni-Cr were prepared and preplaced one over another (thickness of each composition layer was around 300im) on the surface of AISI 316L SS. The preplaced graded coatings were melted with laser radiation with different powers (3.3 & 2.0 kW) and scan speeds (1.0, 2.0 & 3.0 m/min.) This study showed the formation of two distinct layers (with and without microstructure) when the laser power was 2 kW and scan speeds were 1.0 & 2.0 m/min. When the scan speed was 3.0 m/min., intermixing of layers was observed. Mixing of layers was prominent when the power was 3.3 kW (scan speeds 3.0 & 2.0 m/min). When the scan speed was 1.0 m/min, complete mixing of layers (homogeneous alloying) was observed. The layers without and with microstructure exhibited microhardness in the range of 1400-1500 HV and 170-250 HV, respectively. The microhardness near the surface of the complete alloyed region was about 250 HV up to a depth of 50 microns and after that 700-900HV up to the alloy-substrate interface (depth 650 microns). The hardness obtained in the complete alloyed region is about 4 times of the AISI 316L SS substrate. The paper also discusses different phases formed during laser melting and distribution of elements in the laser melted regions.

Texture and Microstructure in Thin Films and Coatings: Techniques and Coatings

Sponsored by: ASM International: Materials Science Critical Technology Sector, ASM/MSCTS-Texture & Anisotropy Committee
Program Organizers: David P. Field, Washington State University, Pullman, WA 99164-2920 USA; Chris A. Michaluk, Williams Advanced Materials, Gilbertsville, PA 19525 USA; John E. Sanchez, Advanced Micro Devices, Sunnyvale, CA 94088 USA; J. A. Szpunar, McGill University, Department of Metallurgical Engineering, Montreal, Quebec H3A 2A7 Canada

Monday PM Room: 3010
February 14, 2005 Location: Moscone West Convention Center

Session Chairs: Hualong Li, ResMat Corp., Montreal, Quebec H3A 2B3 Canada; Masashi Watanabe, Lehigh University, Bethlehem, PA 18015 USA

2:00 PM Invited
In-Fab Control of Texture and Microstructure in Microelectronic Devices: *Kris Jan Kozaczek*[1]; [1]Hypernex, Inc., 3006 Rsch. Dr., State College, PA 16801 USA

Microstructural features such as phase composition, crystallographic texture, and grain size distribution affect the adhesion, stress voiding, electromigration resistance, and electrical resistivity of thin films and interconnects used in 90 nm and 65 nm technologies. The off- and in-line R&D efforts allow one to optimize the microstructure for film and interface properties, and ultimately for improved performance. One of the tools used in-line for microstructure tailoring is an automated x-ray diffraction (XRD). We will show the examples of in-fab applications of XRD tools capable of mapping 200 and 300 mm wafers for phase, grain size, and texture with throughout rates up to 40 wafers per hour. Current deposition and processing techniques such as CVD, PVD, electroplating, annealing, and electro-mechanical polishing provide numerous opportunities for microstructure control throughout the fabrication process. Adversely, tool instability or process excursions are reflected in microstructural deviations across one wafer or from wafer to wafer. XRD has been successfully applied in the leading semiconductor fabs to establish the processing-microstructure-property relationships, and as a process monitor sensitive to deposition conditions. The examples will focus on a typical processing route in fabrication of damascene copper interconnects. Additional applications in metal gate processing and in manufacture of ferroelectric memory devices will be presented.

2:30 PM
Practical Comparison of Orientation Determination Techniques in Transmission Electron Microscopy: *Masashi Watanabe*[1]; David B. Williams[1]; [1]Lehigh University, Dept. of Matls. Sci. & Engrg., 5 E. Packer Ave., Bethlehem, PA 18015 USA

Electron backscatter diffraction (EBSD) techniques in scanning electron microscopy (SEM) can automatically measure and visualize individual crystallographic orientations of grains in polycrystalline materials. This approach is more efficient than conventional electron diffraction in transmission electron microscopy (TEM) because sample preparation for SEM-EBSD is much easier (no need for electron-transparent thin films) and much larger areas can be examined relatively quickly. However, TEM approaches are still useful because the spatial resolution is higher than SEM-EBSD and crystallographic relationships between grains can be correlated directly with chemistry around the grain boundaries. Recently, several automated orientation-determination techniques have become available in TEM: e.g. automatic crystallography for TEM (ACT) and orientation determination based on a convergent beam electron diffraction method. In this study, the TEM-based orientation-determination techniques will be compared practically in terms of accuracy and usefulness in misorientation measurements between grains in thin-film specimens.

2:50 PM
Depth-Resolved Internal Strain and Texture in Coatings Using Micro-Focused High-Energy X-Rays: *Jonathan Almer*[1]; Magnus Oden[2]; [1]Argonne National Laboratory, Advd. Photon Source, 9700 S. Cass Ave., Bldg. 431, Argonne, IL 60439 USA; [2]Lulea University of Technology, Engrg. Matls., Sweden

We investigate internal strain, microstructure and texture in physical-vapor-deposited (PVD) metal nitride coatings TiN and CrN. The non equilibrium nature of the PVD process leads to high defect densities and internal stresses in these coatings. We describe a new technique, using high-energy synchrotron x-rays, focusing optics and an area detector, which allows strain and texture for multiple crystallographic planes to be measured by a single x-ray exposure. The coatings are measured in a cross-sectional transmission geometry, rather than the (traditional) reflection geometry. The depth resolution is therefore direct and given by the x-ray beam size (down to one micron), rather than cumulative as in reflection-based methods. Unique texture states, nonlinear strain-orientation distributions and strain gradients are observed for different coatings. These observations are compared with existing micromechanical models and correlated with deposition conditions. This work was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. W-31-109-Eng-38.

3:10 PM
Grain Boundary Energy as a Function of Misorientation in <111> Fiber-Textured Al Films: Experiment and Computation: *Katayun Barmak*[1]; Jihwan Kim[1]; Chang-Soo Kim[1]; Gregory S. Rohrer[1]; Anthony D. Rollett[1]; Hao Zhang[2]; David J. Srolovitz[2]; [1]Carnegie Mellon University, Dept. of Matls. Sci. & Engrg., 5000 Forbes Ave., Pittsburgh, PA 15213 USA; [2]Princeton University, Dept. of Mechl. & Aeros. Engrg., Princeton Inst. for the Sci. & Tech. of Matls., Princeton, NJ 08540 USA

Electron back scatter diffraction and a statistical multiscale method have been used to determine the relative boundary energy as a function of misorientation at more than ten-thousand triple junctions in <111> textured Al films. The films are 1.7 microns thick and are sputter deposited onto oxidized silicon and annealed at 450°C for 5 hours. The large data set of more than ten thousand junctions has allowed the relative boundary energies to be determined with a 2° resolution in misorientation. The strong texture allied with a nearly columnar grain structure means that almost all of the boundaries have tilt character and a common <111> axis. The experimental energies are compared with energies computed with atomistic (molecular dynamics) simulations of migrating boundaries in bi-crystals. A potential appropriate to Al is used. Good agreement between the experimental and computed energies is found with cusp-shaped minima at the same locations.

3:30 PM Break

4:00 PM
Effect of Heat Treatment on Texture of Zirconium Oxide Thin Film Grown on Zr-2.5Nb Substrates: Jianlong Lin[1]; Hualong Li[1]; *Jerzy A. Szpunar*[1]; [1]McGill University, Dept. of Metals & Matls. Engrg., M.H. Wong Bldg., 3610 Univ. St., Montreal, PQ H3A 2B2 Canada

Zirconium oxide thin film grown on Zr-2.5Nb alloy substrates acts as a barrier against further corrosion and hydrogen permeation in nuclear reactors. The effect of texture of zirconium substrates on the development of the texture of the oxide thin film was investigated. Heat treatment was applied to Zr-2.5Nb substrates in order to modify the microstructure and texture of the substrates. Texture of the substrates and the oxide film was measured and ODF was calculated from the measured pole figures data. The results show that the texture of the oxide film is affected by the texture of substrates. A study was undertaken to investigate the oxidation kinetics in 500°/C air environment on heat treated substrates and as-received Zr-2.5Nb substrate. It is found that the texture of the oxide film is related to the texture of the substrates and oxidation kinetics of the Zr-2.5Nb alloy is affected by the heat treatment history on the substrates and oxide microstructure and texture. SEM was employed to investigate the substrates and oxide morphology. The result obtained indicated that the morphology of the oxide film is related to the amount of ?Ò-phase in the substrates.

4:20 PM
Process-Microstructure Relationship of AlN Layers Produced by Reactive Magnetron Sputtering: Ulises Figueroa[1]; *Olimpia Salas*[1]; Joaquín Oseguera[1]; [1]ITES-CEM, Ingeniería Mecánica y Mecatrónica, Carretera a Lago de Guadalupe km. 3.5, Atizapán, México 52926 México

AlN PVD layers deposited on glass substrates by reactive magnetron sputtering under various conditions were investigated. The main processing variables were: gas mixture working pressure and substrate to target distance. The resulting films were analyzed by Scanning Electron Microscopy + Energy Dispersive x-ray Microanalysis, x-ray diffractometry and Transmission Electron Microscopy. Observations indicate that the characteristics of these films: residual stress, growth morphology and surface roughness are influenced mainly by working pressure and target to substrate distance.

The Armen G. Khachaturyan Symposium on Phase Transformation and Microstructural Evolution in Crystalline Solids: Session II

Sponsored by: Electronic, Magnetic & Photonic Materials Division, Materials Processing & Manufacturing Division, EMPMD/SMD-Chemistry & Physics of Materials Committee, MPMD-Computational Materials Science & Engineering-(Jt. ASM-MSCTS), MPMD-Phase Transformations Committee-(Jt. ASM-MSCTS)
Program Organizers: Yunzhi Wang, Ohio State University, Department of Materials Science and Engineering, Columbus, OH 43210 USA; Long-Qing Chen, Pennsylvania State University, Materials Science and Engineering Department, University Park, PA 16802-5005 USA; John William Morris, University of California, Department of Materials Science and Engineering, Berkeley, CA 94720 USA

Monday PM Room: 3003
February 14, 2005 Location: Moscone West Convention Center

Session Chairs: Perry H. Leo, University of Minnesota, Aeros. Engrg., Minneapolis, MN 55408 USA; Yu U. Wang, Virginia Tech, MSE, Blacksburg, VA 24061 USA

2:00 PM Opening Remarks

2:05 PM Invited
Nanoscale Phenomena in Synthetic Functional Oxide Heterostructures: *R. Ramesh*[1]; [1]University of California, Dept. of Matls. Sci. & Engrg. & Dept. of Physics, Berkeley, CA 94720 USA

In 1990, I started a basic science program at Bellcore that was aimed at creating model perovskite oxide heterostructures using ferroelectrics as a case study. Our original goal was to study the rather enigmatic problem of polarization fatigue using epitaxial films as model systems. However, in the process of doing so, we discovered a novel solution to this problem, namely the use of conducting oxide electrodes as contacts rather than conventional metals such as Pt. The key here, of course, is the atomic scale microstructure of electrical interfaces in the ferroelectric capacitor. A considerable amount of intellectual property based on this invention has been generated and is currently being licensed for development and manufacture. Over the past several years at Maryland, we have focused considerable effort on understanding the growth and characterization of functional oxide thin films and heterostructures, specifically ferroelectric, dielectric and magnetic perovskites. Using both epitaxial and polycrystalline materials on a variety of substrates as test vehicles, we have been carrying out systematic studies on the effect of composition, point defect chemistry, strain and processing variables on the microstructure and physical properties. One novel aspect of our work is the combined use of focused ion beam milling and scanning force microscopy techniques to understand the influence of film microstructure on the relevant properties at the nanoscale, specifically domains in epitaxial films and mapping of their dynamics at the nanoscale using scanned force microscopy. This, in conjunction with the implementation of a variety of novel probes, including scanning microwave microscopy, femtosecond optical probes of polarization dynamics, as well as a comprehensive theoretical treatment (both first principles and continuum mechanics) has provided us with an interdisciplinary approach to understanding complex dynamical phenomena in these materials. I will focus on some of our recent observations on nanoscale phenomena in ferroelectric thin films using scanned probes. In this presentation, I will describe some possible areas where fundamental measurements in conjunction with theoretical studies and modeling will enable a better understanding of the complex phenomena involved in these materials, especially the role of structural, chemical and functional interfaces (such as domain walls). The work at Maryland is supported by the NSF-MRSEC.

2:30 PM Invited
The Morphology and Directed Self Assembly of Quantum Dots on Surfaces: O. Shklyaev[2]; M. Beck[1]; K. Thornton[3]; M. D. Asta[1]; M. J. Miksis[2]; *P. W. Voorhees*[1]; [1]Northwestern University, Matls. Sci. & Engrg., 2220 Campus Dr., Cook Hall, Evanston, IL 60208 USA; [2]Northwestern University, Engrg. Sci. & Appl. Math., Evanston, IL 60208 USA; [3]University of Michigan, Matls. Sci. & Engrg., Ann Arbor, MI USA

Armen Katchaturyan has had a long interest in the effects of stress on the evolution of interfaces. Here we discuss the important role of elastic stress on the evolution of island morphology, or quantum dots, on surfaces. We first discuss the formation of a Ge island on a Si substrate. We combine first-principles calculations of the stress dependence of the Ge (105) and Si (100) surface energies along with an analytical formulation of the elastic strain energy of pyramidal islands. We find that the dependence of the surface energy on strain plays an unexpectedly large role in the energetics of island formation. Directed self assembly is a promising route to controlling the location of islands on surfaces during heteroepitaxy. The results of three-dimensional phase field calculations of the directed self assembly on templated substrates with various morphologies will be given.

2:55 PM Invited
Modeling Microstructure Formation Using Phase Field Crystals: *Ken R. Elder*[1]; [1]Oakland University, Physics, Rochester, MI 48309 USA

The vast majority of naturally occurring or man-made solids are not in equilibrium and contain complex spatial structures on nanometer, micron or millimeter length scales. This is particularly important since these morphologies often determine the mechanical, electrical and optical properties of the material. Elastic and plastic deformations frequently have a significant impact on the nature of the morphologies, but are difficult to incorporate in theoretical treatments. In this talk I would like to discuss the use of phase field crystals to model elastic and plastic deformations in microstructure formation in pure and binary systems. For illustrative purposes a number of applications will be considered including liquid phase epitaxial growth, spinodal decomposition, eutectic solidification, dendritic growth and material hardness.

3:20 PM
Long-Time Dynamics of Biaxially Stressed Solid Surfaces: *Jerome Paret*[1]; [1]L2MP - CNRS UMR 6137, Faculté des Sciences de St. Jerome, Case 142, Marseille 13397 France

Using a phase-field model including strain fields, we numerically investigate the dynamics of a biaxially stressed solid surface. A multigrid algorithm is used to solve the elastic part of the problem. Its efficiency allows us to explore for the first time the late stages of the full 3D Grinfeld instability. Recent analytical predictions [P. Berger et al., Phys. Rev. Lett. 90, 176103 (2003)] regarding stability and selection of patterns are confirmed. It appears that, in presence of a large scale stabilization mechanism, the system reaches an equilibrium state corresponding to a non-trivial striped pattern.

3:35 PM Break

4:00 PM Invited
Numerical Simulations of Pattern-Directed Phase Decomposition in Stressed Films: *S. M. Wise*[1]; J. S. Lowengrub[1]; J. S. Kim[1]; W. C. Johnson[2]; [1]University of California, Math. Dept., Irvine, CA 92697-3875 USA; [2]University of Virginia, Dept. of Matls. Sci. & Engrg., Charlottesville, VA USA

A Cahn-Hilliard evolution equation possessing a source term is employed to study the morphological evolution of a strained heteroepitaxial thin film, during continuous mass deposition, on a substrate with an embedded coherent island. Both the elastic properties and the surface energy of the film are anisotropic. A sophisticated multigrid method and an implicit time integration scheme are combined to make an efficient numerical method, one which enables numerically tractable computation in both two and three dimensions. Herein we present preliminary two-dimensional results of our work showing feasibility of both the model and numerical method. This work is supported by the U.S. National Science Foundation through the Center for the Design of Nanoscopic Materials.

4:25 PM
Modeling of Self-Assembling Nano-Structures in Thin Constrained Layers.: *Andrei Artemev*[1]; Alexander L. Roytburd[2]; Julia Slutsker[3]; [1]Carleton University, Mech. & Aeros. Engrg., 1125 Colonel By Dr., Ottawa, ON K1S 5B6 Canada; [2]University of Maryland, Matls. Sci. & Engrg., College Park, MD 20742 USA; [3]National Institute of Standards & Technology, Gaithersburg, MD 20899 USA

The formation of patterns produced by misfitting coherent domains in thin constrained layers was studied using the phase-field method based on microelasticity theory. Simulation was performed for (i) multivariant systems in which misfit strain can be accommodated by assembling domains of different orientation variants and (ii) for monovariant systems. Different types of regular patterns were obtained including columnar, striped, labyrinth, and lattice patterns. The effects of thickness of polydomain layer, misfit between domains, and misfit with monodomain constraining layer on the patterns were studied. The structure maps illustrating conditions at which different types of structure can be obtained were produced. The results of computer

simulation were compared with simplified analytical models of domain structures in constrained layer.

4:50 PM
Theory and Modeling of Spinodal Decomposition in Constrained Films: *Julia Slutsker*[1]; Andrei Artemev[2]; Alexander L. Roytburd[3]; [1]National Institute of Standards & Technology, Matls. Sci. & Engrg., 100 Bureau Dr., Gaithersburg, MD 20899 USA; [2]Carleton University, Mech. & Aeros., Ottawa Canada; [3]University of Maryland, Matls. Sci. & Engrg., Coll. Park 20742 USA

The theory and phase field modeling is developed for analysis of the compositional and structure transformations in constrained layer. The equation of TDGL is used for simulation of a structural transformation, and Cahn-Hillard equation is used for simulation of a concentration decomposition. The initial state in both cases is unstable and decomposition of an uniform film results in formation of an equilibrium two- phase mixture consisting of the phases with different values of the order parameter or concentrations. Period and morphology of two-phase structure depend on the thickness of the film and misfit between film and substrate layer. The results of the simulation are compared with experimental observations in multiferroic nano-structures and polydomain structures of ferroelectrics.

5:05 PM
Next-to-Nearest Neighbor Interaction and Equilibrium Properties of Steps on Kossel Crystal Vicinal Surface: Vasiliy B. Korsakov[1]; *Robert A. Suris*[1]; [1]A.F. Ioffe Physico-Technical Institute, Polytekhnicheskaya 26, St. Petersburg 194021 Russia

The simplest discrete model of monoatomic step on crystal surface is the step on (100)-surface of cubic Kossel crystal, where atoms interact only with its nearest and next-to-nearest neighbors (NN and NNN respectively). The complete analytical description of such a step was given by Burton, Cabrera and Frank (BCF) more than 50 years ago. The BCF approach is based on the kink statistics formalism and, in principle, completely describes equilibrium properties of a step without "overhangs". Unfortunately, in general case of arbitrary step direction this description is quite cumbersome and does not allow to "feel" step properties. We investigate steps, inclined relative to [10] direction, in particularly, [11]-step. We show that if inclination is sufficiently large, one can neglect not only overhangs, but also "negative" kinks. The prohibition of negative kinks radically simplify BCF formalism and allow to obtain essential properties of "inclined" steps in simple analytical form. We show that equilibrium structure of such steps is determined only by the interaction between NNN. If this interaction is repulsive, the step has saw-like shape, while attractive interaction leads to straightening of the step. Kink size distribution, step diffusivity and step free energy are obtained as functions of step inclination and NNN interaction energy. Also we extend BCF formalism to the case of arbitrary, non-pairwise interactions, if only these interactions are limited to the nearest and next-to-nearest neighbors.

5:20 PM
Diffusion in Crystalline Composition-Modulated Films: *Alan F. Jankowski*[1]; [1]University of California/Lawrence Livermore National Laboratory, CMS - Matls. Sci., PO Box 808, MS L-352, Livermore, CA 94551-9900 USA

The diffusivity in alloy systems at low temperatures is determined using composition-modulated structures. An artificial concentration wave is produced by alternating a deposition of the alloy elements. A quantification of the interdiffusivity coefficient is determined by analyzing the decay of the composition fluctuation, that is, the static concentration wave using the microscopic theory of diffusion. As it is customary to assume that there is a linear relationship between ln D and 1/T over a wide range of temperature, the bulk diffusion coefficient represents the long wavelength approximation of the interdiffusivity. The dependency of interdiffusivity on structure is found in general expressions that account for the specific periodicity and growth orientation of the multilayer structure. The kinetics are quantified by analyzing changes in the composition fluctuation through x-ray scattering measurements. In addition to the examination of single-phase crystalline systems as Cu-Ni and Cr-Ti, the approach is now developed to assess two-phase layered systems. Specifically, as in Ni-(Cr,Mo) where a face-body centered cubic combination form a pseudo epitaxial system.

The Langdon Symposium: Flow and Forming of Crystalline Materials: High Temperature Deformation Including Superplasticity

Sponsored by: Materials Processing & Manufacturing Division, Structural Materials Division, MPMD-Shaping and Forming Committee, SMD-Mechanical Behavior of Materials-(Jt. ASM-MSCTS)

Program Organizers: Yuntian Ted Zhu, Los Alamos National Laboratory, Materials Science and Technology Division, Los Alamos, NM 87545 USA; P. B. Berbon, Rockwell Scientific Company, Thousand Oaks, CA 91360 USA; Atul H. Chokshi, Indian Institute of Science, Department of Metallurgy, Bangalore 560 012 India; Z. Horita, Kyushu University, Department of Materials Science and Engineering, Fukuoka 812-8581 Japan; Sai V. Raj, NASA Glenn Research Center, Materials Division, Cleveland, OH 44135 USA; K. Xia, University of Melbourne, Department of Mechanical and Manufacturing Engineering, Victoria 3010 Australia

Monday PM — Room: 3024
February 14, 2005 — Location: Moscone West Convention Center

Session Chairs: Eric M. Taleff, University of Texas, Dept. of Mechl. Engrg., Austin, TX 78712-0292 USA; Tadao Watanabe, Tohoku University, Dept. of Nanomech., Sendai, Miyagi 980-8579 Japan; Farghalli A. Mohamed, University of California, Cheml. Engrg. & Matls. Sci., Irvine, CA 92697-2575 USA; Norio Furushiro, Osaka University, Internatl. Student Ctr. & Dept of Matls. Sci. & Engrg., Grad. Sch. of Engrg., Suita, Osaka 565-9871 Japan

2:00 PM
Effect of Nano-Dispersion Particles on Superplastic Flow in Zn-22% Al: *Farghalli A. Mohamed*[1]; Yuwei Xun[1]; [1]University of California, Cheml. Engrg. & Matls. Sci., 916 Engrg. Tower Bldg., Irvine, CA 92697-2575 USA

A detailed creep investigation was performed on Zn-22%Al in which nano-scale dispersion particles were introduced by cryomilling. The objective of the investigation was to determine the effect of these dispersion particles on creep and microstructure in region I and region II of the sigmoidal plot between stress and strain rate, which was previously reported for the alloy. The results show that while the particles have no significant effect on the sigmoidal plot, their presence influences several characteristics in region I. An examination of creep microstructures in region II and region I reveals that only some grains contain dislocations, many of which are attached to the dispersion particles. On the basis of these results and other available information, it is concluded that region I and region II are controlled by the same deformation process, in which the sliding of groups of grains is accommodated by dislocation motion in the blocking grains.

2:15 PM
Elongation to Failure in the Model of Cooperative Grain Boundary Sliding: *Oscar Akramovich Kaibyshev*[1]; Anatoliy Ivanovich Pshenichnyuk[1]; [1]Institute for Metals Superplasticity Problems, 39 Khalturin str., Ufa, Bashkortostan 450001 Russia

In recent papers[1,2] we presented the model of the superplastic deformation (SPD), which postulates the cooperative grain boundary sliding (CGBS) as a principal mechanism of deformation. The model shows that the SPD occupies the interval of s (or) values between diffusion and dislocation creep. However, the SPD is not a mere combination of these processes but presents a separate phenomenon and is realised by a specific deformation mechanism - the CGBS. The stresses, which set the lower and the upper limits of the SPD stress interval, are not imposed artificially but are derived from the condition of CGBS bands development. The threshold stress depends on the temperature, mean grain size, variance of size distribution and the value of the percolation level. The model adequately describes s- dependencies for the SPD in real materials. On the base of those results we simulated the elongation to failure. The calculation is based on the concept of cooperative grain-boundary sliding and consists of solving the equation: where 2r (z,t) is the cross-sectional width at time t and a space coordinate z (-l(t)<z<l(t)), VB is the rate of shear in a separate band, n (z,t) is a random function describing the spatial distribution of the CGBS bands along the specimen at time t. Nonuniformity of CGBS band spatial distribution, which was created randomly during deformation, leads to flow localization on macro-level. An analysis of the statistical properties of the random function n(z,t) allows us to define deformation to failure and its dependence on the strain-rate, mean grain size

and samples geometry. [1]O.A. Kaibyshev, A.I. Pshenichnyuk, V.V. Astanin. Acta mater., 46(1998)4911. [2]A.I.Pshenichnyuk, O.A. Kaibyshev, V.V. Astanin. Phil. Mag. A79(1999)329.

2:30 PM
Cavitation Failure in Superplasticity: *Atul H. Chokshi*[1]; [1]Indian Institute of Science, Metall. Dept., Bangalore 560012 India

Although most early studies on superplasticity examined failure largely in terms of stability of plastic flow against flow localization, it is now recognized that concurrent cavitation plays a dominant role in the failure of many superplastic alloys. Professor Langdon was amongst the first to recognize the importance of cavitation in the failure of superplastic materials. This paper will briefly review various important aspects on cavity nucleation, growth and interlinkage in a wide range of superplastic materials from conventional microduplex metallic alloys to ceramics, and it will highlight techniques developed to retard cavitation during industrial superplastic forming.

2:45 PM
Material Modelling Data for Superplastic Forming Optimisation: *Norman Ridley*[1]; Pete S. Bate[1]; Baoliang Zhang[1]; [1]University of Manchester, Matls. Sci. Ctr., Grosvenor St., Manchester M1 7HS UK

Optimisation of the superplastic forming process involves the determination of the minimum forming time within the constraints of product characteristics such as thickness distribution and cavitation level. However, superplastic forming is a non-linear system, with the material behaviour giving a significant contribution to that non-linearity. For example, dynamic grain growth gives useful strain hardening but can ultimately reduce strain rate sensitivity, and conversely forming with a decreasing strain rate can enhance ductility. Superplastic materials can also exhibit plastic anisotropy. The results of tests on two commercial superplastic alloys, AA5083 and AA7475, have been used to provide data for material modelling. Simple power law descriptions of the mechanical behaviour were not adequate, and constitutive relationships for these materials are presented and discussed.

3:00 PM
Superplasticity in Ceramics with Intergranular Phases: *Martha L. Mecartney*[1]; [1]University of California, Cheml. Engrg. & Matls. Sci., 916 Engrg. Tower, Irvine, CA 92697-2575 USA

Highly deformable, fine grain oxide ceramics can be created using intergranular phases to limit grain growth and promote superplastic behavior. Cubic zirconia (8 mol% Y2O3 stabilized ZrO2, 8Y-CSZ) can be deformed over 500% in tension at 1430°C with the addition of 5 wt.% intergranular silica. A mixture of 5 wt.% SiO2 and 1 wt.% Al2O3 in 8Y-CSZ can achieve strain rates of 0.0002/sec at 1200° C and 30 MPa stress. Alumina based composites can achieve high strain rates of 0.01/sec (1500°C, 50 MPa stress) with the combined addition of intergranular silica and zirconia. Al2O3 composites with 10 vol.% ZrO2 and 0.5 mol% of the intergranular phase CuO/Mn3O4 have demonstrated deformation rates of 0.001 at 1300°C under 30 MPa stress. This talk will summarize how intergranular phases can be used to achieve the goal of high strain rate superplasticity in ceramics.

3:15 PM
A Unified Tensile Test to Define the Superplastic Properties of Materials: *Peter N. Comley*[1]; [1]The Boeing Company, PO Box 3707, m/c 5K-63, Seattle, WA 98390 USA

The testing methods and presentation of SPF data have encompassed a wide spectrum of techniques, and results can differ from one test to another. In particular, distortion of the coupon during testing, the difficulty of measuring strain in the gauge length, the translation of constant crosshead velocity to strain rate, and other factors, have all disguised or distorted the true superplastic properties of materials. This paper proposes a specification to define the correct superplastic properties of any material. It addresses the shape of the coupon to minimize errors of measurement, the application of constant strain rate, the generation of true stress and true strain, the format that data should be presented, and the generation of "m" and "n" values. It is hoped that this could become the basis of a world standard SPF test that both academic and industrial institutions can use.

3:30 PM
A Comparative Study of Cavitation Characteristics in Superplastic 5083 Al and AZ31 Mg Alloys: Yasumasa Chino[1]; *Hajime Iwasaki*[1]; Mamoru Mabuchi[2]; [1]National Institute of Advanced Industrial Science and Technology, Matls. Rsch. Inst. for Sustainable Dvlp., 2266-98 Shimo-Shidami, Moriyama-ku, Nagoya 463-8560 Japan; [2]Kyoto University, Dept. of Energy Sci. & Tech., Kyoto 606-8501 Japan

The plasticity-controlled growth rate of cavities during superplastic deformation was statistically investigated for 5083 Al alloy and AZ31 Mg alloy. When the cavity growth rate was evaluated on the basis of macroscopic strain calculated using the displacement of the specimen, the growth rate for the Al alloy was larger than that for the Mg alloy. However, the growth rate of the Al alloy was in agreement with that of the Mg alloy when the cavity growth rate was evaluated on the basis of the microscopic strain due to grain boundary sliding. The results obtained lead to two conclusions: (1) the rate of cavity growth is not affected by the kind of materials, that is, the nature of the grain boundary and (2) the microscopic strain due to grain boundary sliding should be used to exactly evaluate the rate of cavity growth for superplastic deformation.

3:45 PM
Change in Crystallographic Distribution During Superplastic Deformation in an Al-Zn-Mg-Cu Alloy: Yoshimasa Takayama[2]; *Norio Furushiro*[1]; [1]Osaka University, Internatl. Student Ctr. & Dept. of Matls. Sci. & Engrg., Grad. Sch. of Engrg., 1-1 Yamadaoka, Suita, Osaka 565-9871 Japan; [2]Utsunomiya University, Dept. of Mechl. Sys. Engrg., 7-1-2, Yoto, Utsunomiya, Tochigi 321-8585 Japan

The change in crystallographic orientation distribution during superplastic deformation in an Al-Zn-Mg-Cu alloy has been investigated in order to reveal the deformation mechanism. The well known strain rate dependence of the deformation behavior was examined by SEM/EBSP (scanning electron microscope/electron back scatter diffraction patter) analysis. Fraction of low angle grain boundaries increased after deformation at the high strain rate, while fraction of random boundaries was high in the specimen deformed at the low strain rate. Randomization of the initial texture was also found during deformation at the low strain rate. Further, the intragranular misorientation, grain boundary misorientation and local orientation are analyzed in detail to discuss the accommodation process.

4:00 PM Break

4:15 PM
High Temperature Deformation and Fracture Controlled by Grain Boundaries: *Tadao Watanabe*[1]; Sadahiro Tsurekawa[1]; Shigeaki Kobayashi[2]; Shin-ichi Yamaura[1]; [1]Tohoku University, Dept. of Nanomech., Sendai, Miyagi 980-8579 Japan; [2]Ashikaga Institute of Technology, Dept. of Mechl. Engrg., Faculty of Engrg., Ashikaga, Tochi Japan

Grain boundaries can play important roles in deformation and fracture in bicrystals and polycrystals at high temperatures where grain boundary phenomena become dominant. It has been well established thatgrain boundary phenomena strongly depend on the type and structure of grain boundary.[1] So it is indispensable to understand how different grain boundary phenomena interact to each other to enhance or supress plastic deformation and fracture of polycrytstalline materials at high temperatures. This paper is an overview of recent studies of structure-dependent grain boundary phenomena which are involved in high temperature deformation and fracture in polycrystalline materials. Recent applicationsof grain boundary engineering to the control of intergranular brittleness,[2] oxidation brittleness[3] and also development of superplasticity[4] will be discussed. [1]T.Watanabe, Metall.Trans., A14(1983),531; [2]T.Watanabe, Mater.Sci.Eng., A166(1993), 11; [3]S.Yamaura, S.Tsurekawa and T.Watanabe, Mater.Trans.44(2993), 1497; [4]S.Kobaayashi, T.Yoshimura,S.Tsurekawa and T.Watanabe, Mater.Trans.,44(2003),1469.

4:30 PM
Elevated Temperature Deformation: Hot Working Amplifies Creep: *Hugh J. McQueen*[1]; Michael E. Kassner[2]; [1]Concordia University, Mechl. Engrg., 1455 Maisonneuve W., Montreal, QC H3G 1M8 Canada; [2]University of Southern California, Aeros./Mechl. Engrg., Los Angeles, CA 90089-1453 USA

Because creep research is motivated by restricting high temperature T strain ε, it generally considers rates below 0.0001/s and low ε defined by tensile failure or by minimum rate in compression. Hot working (0.01-100/s) studies aim to reduce hot strength and raise fracture ε in deformation modes extending far into steady state. While dependence of stress σ and substructure character in steady state are similarly linked to T and ε rate through dynamic recovery (DRV), the high ε permits evolution unrecognized in creep, even geometrically refining the grains to the subgrain size and aligning them into intense textures. The higher σ leads to higher misorientations that in multistage processing gives rise to static recrystallization to lower forces, improve ductility and refine structure. Although grain boundary (GB) sliding declines to less than 1% of total ε at high rates, it is the inherent cause of failure; nevertheless, accommodation of sliding at triple junctions by DRV-enhanced grain flow provides torsional ε exceeding 100.

In Al-5Mg, solute drag on dislocations constrains subgrain formation to larger ε with sizes smaller and stresses higher by a factor of 4; yet elongations are similarly multiplied due to augmented strain rate sensitivity. In low stacking fault energy metals, dynamic recystallization refines grains, lowers strength and raises ductility as GB migration lowers σ concentrations at triple junctions and retards cracking. In thermomechanical processing, substuctures can be developed for strength with toughness, creep resistance in superalloys, or conversion to superplastic behavior.

4:45 PM

Effect of Thermo-Mechanically Induced Microstructural Coarsening on the Evolution of Creep Response of SnAg-Based Microelectonic Solders: Robert A. Marks[2]; Deng Pan[1]; Susheel Jadhav[3]; *Indranath Dutta*[1]; [1]Naval Postgraduate School, Ctr. for Matls. Sci. & Engrg., Dept. of Mechl. & Astronautical Engrg., 700 Dyer Rd., Monterey, CA 93943 USA; [2]University of California, Dept. of Matls. Sci. & Engrg., Berkeley, CA 94720 USA; [3]INTEL Corporation, Assembly Tech. Dvlp., 5000 W. Chandler Blvd., CH5-165, Chandler, AZ 85226 USA

Microelectronic solder joints, which serve as both electrical and mechanical connections between a chip and various parts of a package, are subjected to aggressive thermo-mechanical cycling (TMC) during service, with shear strains and homologous temperatures reaching up to 1 and 0.9, respectively. As a result, the creep behavior of the tiny solder joints limits the reliability of the entire microelectronic package. In addition, the microstructures of the new lead-free solders (Sn/Ag and Sn/Ag/Cu) can undergo significant in situ strain-enhanced coarsening during TMC, resulting in in-service evolution of the creep behavior of the joints. In these materials, Ag3Sn and Cu6Sn5 precipitates can serve as barriers to dislocation motion, and thus, influence creep behavior, dependent on the particle size and spacing. In this paper, the coarsening kinetics of Ag3Sn particles in Sn/Ag-based microelectronic interconnects is presented, and the results are correlated with impression creep data from individual microelectronic solder balls subjected to particle-growth anneals. Coarsening influences creep behavior in two ways. At low stresses, the creep rate increases proportionately with precipitate size. At high stresses, as proposed by Langdon, precipitate coarsening influences creep response by altering the threshold stress for particle-limited creep. Based on these observations, a creep model for solder interconnects undergoing in situ coarsening is presented. Supported by NSF, SRC and INTEL Corp.

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Deformation Behavior of Mg-Li Alloys at Elevated Temperatures: *Zuzanka Trojanova*[1]; Zdenek Drozd[1]; Pavel Lukac[1]; Frantisek Chmelik[1]; [1]Charles University, Dept. of Metal Physics, Ke Karlovu 5, Praha 2 12116 Czech Republic

Magnesium alloys are attractive for a large amount of applications. It is important to estimate the deformation mechanisms responsible for the deformation behaviour of Mg alloys at elevated temperatures. Experiments were conducted to evaluate the influence of the testing temperature and strain rates on the deformation behaviour. The tests were performed using Mg-4 wt. % Li (Mg-12 at. % Li) at temperatures between 293 and 473 K and at a constant but different initial strain rate. Stress relaxation tests were carried out in order to estimate parameters of a possible thermally activated process. The results show that the flow stress rapidly decreases with increasing temperature. Softening occurs at higher temperatures and it is attributed to annihilation of dislocations during deformation. The activation volume calculated from the stress relaxation test decreases with strain. This investigation demonstrates that the imposed initial strain rate influences the course of stress-strain curves.

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Analysis of the Effect of Si Content on the Creep Response of a Mg-5Al-Mn Alloy: Stefano Spigarelli[1]; Marcello Cabibbo[1]; Claudia Scalabroni[1]; *Enrico Evangelista*[1]; Pal Ulseth[2]; Otto Lohne[2]; [1]Universita' Politecnica delle Marche, Dept. of Mech., Via Brecce Bianche, Ancona 60131 Italy; [2]NTNU, Dept. of Matls. Tech. & Electrochmst., Trondheim N-7491 Norway

The die-cast AM50 (Mg-5Al-0.5Mn) alloy is used for the production of automotive components and other parts that require good ductility and toughness combined with reasonable tensile strength. However, this material, like many other Mg-alloys including AZ91, has a relatively low creep resistance; on the other hand, the beneficial effect of Si addition in enhancing the creep strength at low stresses, has been clearly observed by comparing the high-temperature behaviour of AZ91, AS21 (Mg-2Al-1Si) and AS41 (Mg-4Al-1Si). In this context the present study aims at investigating the effect of small Si-addition (0.3, 0.5, 0.8 and 1.5%Si) on the creep response of a AM50 alloy. Tensile tests at room temperature and constant load creep tests at 150 and 125°C were carried out on die-cast samples, without any prior-heat treatment. The effect of chemical composition was investigated by testing 5 different alloys with Mg-content increasing from 0 (base AM50 alloy) to 1.5 %. Tensile tests at room temperature indicated that the increase in Si content had a minor effect on strength, but determined a reduction of ductility, a result that was fully consistent with the data available for the conventional AM50 (yield strength 130 MPa, tensile strength 210-225 MPa, elongation 8-10%) and AS41 (yield strength 140 MPa, tensile strength 215 MPa, elongation 6%). Nevertheless, the effect of Si-content was much more pronounced at high temperature. The creep curves, irrespective of the Mg content, consisted in a well defined primary stage, followed by a short secondary region and by a short tertiary stage that led to fracture without extensive necking. A mere 0.3% addition in Mg resulted in an increase of the time to fracture from 23 to 36 h under 100 MPa at 125°C; further Mg-additions produced a substantial increase in creep strength (time to rupture 133 h in the same testing conditions), accompanied by a decrease of strain to fracture. Optical and electron microscopy studies were carried out to investigate the influence of Mg in the creep response; this effect was attributed to the precipitation of Mg2Si particles.

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Effect of Microstructural Variables on Creep Fatigue Resistance in Udimet 720Li: *Philippa Ann Reed*[1]; Hon Tong Pang[1]; Jeff W. Brooks[2]; [1]University of Southampton, Sch. of Engrg. Scis., Highfield, Southampton, Hants SO17 1BJ UK; [2]QinetiQ, Struct. & Matls. Ctr., Cody Tech. Park, Ively Rd., Farnborough, Hants GU14 0LX UK

An assessment of the effects of microstructure on both high temperature crack initiation and propagation of short fatigue and crrepfatigue cracks in a notch stress field in a powder metallurgy turbine disc alloy is presented. The notch was chosen to represent a similar stress concentration feature to that found in the fir-tree root fixing in a turbine disc. The assessment has been carried out on 3 microstructural variants of Udimet 720Li, where grain size and gamma prime size have been varied by sub-solvus heat treatments. Assessment of such behaviour will indicate whether current long crack lifing methodologies (for example based on Paris-type assumptions and long crack growth da/dN versus ?K data) can be extrapolated to such conditions. Comparison of air and vacuum behaviour allows the relative contributions of creep and oxidation in accelerating the fatigue processes to be elucidated.

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Anelastic Creep Behaviour of RR-58 Aluminum Alloy at 180°C: Phenomenological Aspects and Analysis Based on the Unbowing of Dislocation Segments: *Levi de Oliveira Bueno*[1]; [1]Universidade Federal de São Carlos, Dept. de Engenharia de Materiais, Rod. Washington Luiz, km. 235, Caixa Postal 676, São Carlos, SP 13565-905 Brazil

The strain relaxation behaviour after full stress removals during creep of RR-58 Hiduminium alloy has been observed. Creep tests were carried out at 180ºC, with stresses of 120, 170 and 230 MPa. Tests involved a series of unloading cycles after different creep periods involving primary, secondary and tertiary stages. At least two relaxation stages were observed and attempts made to interpret the results according to a model based on thermally activated unbowing of dislocation segments. A suggestion is made for the use of an integrated form of the sine hyperbolic rate equation directly with the readings of anelastic strain and time. Activation parameters are calculated an interpreted considering microstructural details of the material. The appearance of the fast and slow anelastic creep stages may be just a consequence of the high non-linearity relation existing between the line tension and the area swept by the segments during their unbowing movement.