TMS2006

135th Annual Meeting & Exhibition

■ *Linking science and technology for global solutions*

Meeting Information

March 12-16, 2006
Henry B. Gonzalez Convention Center
San Antonio, Texas, USA

Technical Program Follows Meeting Information

You are invited...

Help chart the technological course for future TMS annual meetings, as well as the materials science and engineering profession, by participating in a TMS technical committee. While attending TMS 2006 Annual Meeting & Exhibition, you are invited to attend the technical committee meeting that best serves your area of interest.

Technical Committee Schedule

Sunday, March 12

Pyrometallurgy Committee	10 to 11 a.m.	M	Conference Room 15
Recycling Committee	11 a.m. to noon	M	Conference Room 2
Waste Treatment & Minimization Committee	noon to 1 p.m.	M	Conference Room 16
Thin Films & Interfaces Committee	2 to 3 p.m.	M	Salon M
Process Fundamentals Committee	3 to 4 p.m.	M	Conference Room 15
Aluminum Committee	3 to 5 p.m.	M	Salon E
Copper, Nickel, Cobalt Committee	4 to 5 p.m.	M	Conference Room 5
Lead, Zinc Committee	4 to 5 p.m.	M	Conference Room 8
Nanomechanical Material Behavior Committee	4 to 6 p.m.	M	Conference Room 7
Magnesium Committee	4:30 to 6 p.m.	M	Conference Room 1
Aqueous Processing Committee	5 to 6 p.m.	M	Salon M
Precious Metals Committee	6 to 7 p.m.	M	Conference Room 4
Mechanical Behavior of Materials Committee	6:30 to 8 p.m.	M	Conference Room 16
Materials Characterization Committee	7 to 8 p.m.	M	Conference Room 2
Computational Materials Science & Engineering Committee	7:30 to 8:30 p.m.	M	Conference Room 10
Alloy Phases Committee	7:30 to 9 p.m.	M	Conference Room 8
Phase Transformations Committee	7:30 to 9:30 p.m.	M	Conference Room 5

Monday, March 13

Chemistry & Physics of Materials Committee	7:30 to 8:30 a.m.	M	Conference Room 8
Solidification Committee	12:30 to 1:30 p.m.	M	Conference Room 8
Process Modeling Analysis & Control Committee	12:30 to 2 p.m.	M	Conference Room 6
Advanced Characterization, Testing & Simulation Committee	5:30 to 6:30 p.m.	M	Conference Room 6
Surface Engineering Committee	5:30 to 6:30 p.m.	M	Conference Room 2
Nuclear Materials Committee	5:30 to 7 p.m.	M	Conference Room 10
Composite Materials Committee	5:45 to 7:15 p.m.	M	Conference Room 7
Biomaterials Committee	6 to 7 p.m.	M	Conference Room 11

Tuesday, March 14

Electronic Packaging & Interconnection Materials Committee	7 to 8 a.m.	M	Conference Room 10
Nanomaterials Committee	7:30 to 8:30 a.m.	M	Conference Room 7
Powder Materials Committee	12:15 to 1:45 p.m.	M	Conference Room 10
Reactive Metals Committee	5 to 6 p.m.	M	Conference Room 10
Refractory Metals & Materials Committee	5:30 to 6:35 p.m.	M	Conference Room 12
Shaping & Forming Committee	5:30 to 6:30 p.m.	M	Conference Room 4
Titanium Committee	6 to 7 p.m.	M	Conference Room 16
High Temperature Alloys Committee	6:30 to 8 p.m.	M	Conference Rooms 7

Make Time in Your Schedule for These Programming Features

"The Aluminum Fabrication Industry: Global Challenges and Opportunities"

Monday, March 13, 8:30 a.m. to noon

Dieter Braun, *President, Automotive Sector, Hydro Aluminium Deutschland GmbH, Germany*
"The Importance of the Automotive Industry for the Future Application of Aluminum Components"

Patrick Franc, *President, ARCO Aluminum Inc., USA*
"What are the Challenges and Opportunities for the Rolled Can Sheet Industry?"

Steven Demetriou, *Chairman of the Board & CEO, Aleris International Inc., USA*
"Innovations in Recycling, Continuous Casting and Rolling of Aluminum Products"

Helmut Wieser, *Group President, Alcoa Inc., USA*
"Driving Demand and Cost in a Global Market"

Kevin Greenawalt, *President, Novelis North America, Novelis Corporation, USA*
"Innovative and Sustainable Products for the Aluminum Industry"

Thomas A. Brackmann, *President, Nichols Aluminum, USA*
"The Impact of Alloy Specifications on Aluminum Fabrication and Products - A Future View"

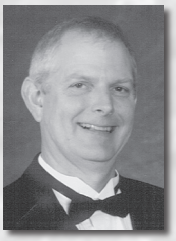
Ding Haiyan, *Board Chairman, Southwest Aluminum (Group) Company Limited; President Assistant, Chinalco, China*
"Developing Aluminum Fabrication in Chinalco: Challenge and Opportunity"

Subodh Das, *President & CEO, Secat Inc., USA*
Moderator


Dieter Braun


Kevin Greenawalt


Patrick Franc


Thomas A. Brackmann


Steven Demetriou


Ding Haiyan


Helmut Wieser


Subodh Das

Rolling, continuous casting and extrusion present many challenges in today's worldwide aluminum fabrication industry. Turning those challenges into opportunities is the subject of this plenary session. Eight corporate leaders from around the world continue the discussion begun at last year's standing-room-only plenary session, "The Role of Technology in the Global Primary Aluminum Industry Today and in the Future," heading downstream from the cast house to the fabricated product in the 2006 session.

"Cast House Operations"

Monday, March 13

Learn from aluminum cast house professionals about the day-to-day technology issues associated with cast house operation, efficiency and quality improvement, including:

- Crack reduction measures
- Energy control
- Scrap rate and scrap flow control
- Alloying and grain refiner practice
- Melt cleanliness
- Cost reduction projects
- Cast quality control (in- and off-line)
- Efficiency improvement projects

"A Century of Nickel Alloy Discovery and Innovation"

Monday, March 13

The year 2006 is the 100th anniversary of the development of Monel metal. To mark this anniversary, this symposium uncovers the history of the development of alloys over the last 100 years:

- Evolution of Wrought Age Hardenable Superalloys
- Evolution of Solid Solution Nickel-Base Alloys for Corrosion Applications
- A Century of Discoveries, Inventors and New Nickel Alloys
- Evolution of Cast Nickel-Base Superalloys
- A Century of Monel Metal 1906-2006

This session concludes with a panel discussion about current material problems and future material requirements in several industries, and a question-and-answer session.

Honor Your Colleagues by Attending These Special Events

Honorary Dinners

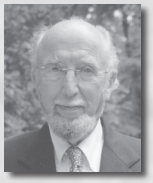
Monday, March 13, San Antonio Marriott Rivercenter Hotel
Dinner tickets must be purchased at the meeting registration desk; no tickets are sold at the door.

Professor John Hunt Honorary Dinner
In conjunction with the symposium "Solidification Modeling and Microstructure Formation: A Symposium in Honor of Professor John Hunt"

Location: Salon B ***Tickets: $65 per person***

Professor Mysore A. Dayananda Honorary Dinner
In conjunction with the symposium "Multi-Component/Multi-Phase Diffusion Symposium in Honor of Mysore A. Dayananda"

Location: Salon C ***Tickets: $55 per person***



Professor Monroe Wechsler Honorary Dinner
In conjunction with the symposium "Wechsler Symposium on Radiation Effects, Deformation and Phase Transformations in Metals and Ceramics"

Location: Salon K ***Tickets: $65 per person***

Professor David Brandon Honorary Dinner
In conjunction with the symposium "The Brandon Symposium: Advanced Materials and Characterization"

Location: Salon D ***Tickets: $65 per person***

Professor Pradeep Rohatgi Honorary Dinner
In conjunction with the symposium "The Rohatgi Honorary Symposium on Solidification Processing of Metal Matrix Composites"

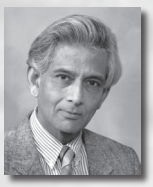
Location: Salon L ***Tickets: $65 per person***

Professor William Gerberich Honorary Dinner
In conjunction with the symposium "Deformation and Fracture from Nano to Macro: A Symposium Honoring W.W. Gerberich's 70th Birthday"

Location: Salon J ***Tickets: $65 per person***

Professor Arthur McEvily Honorary Dinner
In conjunction with the symposium "Fatigue and Fracture of Traditional and Advanced Materials: A Symposium in Honor of Art McEvily's 80th Birthday"

Location: Salon A ***Tickets: $65 per person***



Professor Amiya Mukherjee Honorary Dinner
In conjunction with the symposium "Processing and Mechanical Response of Engineering Materials"

Location: Salon M ***Tickets: $65 per person***

Institute of Metals/Mehl Lecture

"The Promise and Perils of Extreme Grain Refinement to Produce Superior Structural Materials"

Julia R. Weertman

Monday, March 13, 12:30 to 1:30 p.m., Henry B. Gonzalez Convention Center

by Julia R. Weertman, *Department of Materials Science and Engineering, Northwestern University*

About the Topic

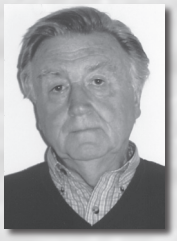
The ability to produce metals with very small grain sizes has led to materials with both the positive aspect of high strength and a number of negative attributes, especially brittle behavior. Attendees of this lecture are updated on the recent developments in the study of the mechanical properties of nanocrystalline metals and alloys, including attempts to make them into useful materials. Julia Weertman's research is sponsored by the Department of Energy Grant DE-FG02-02ER.

About the Speaker

Julia R. Weertman is the Walter P. Murphy Professor Emerita in Service at Northwestern University. At Northwestern for nearly 20 years, she holds three patents and has authored more than 150 technical publications. Weertman has received many professional honors, and is a member of the NRC National Materials Advisory Board.

Hume-Rothery Award Lecture

"Entropies of Formation and Mixing in Alloys"



W. Alan Oates

Monday, March 13
Henry B. Gonzalez Convention Center
Room 202A, Level 2

by W. Alan Oates, *University of Salford, UK*

About the Topic

Attendees learn about:

- Examples in which entropy plays a major role in determining the relative stability of phases in a system at high temperatures
- Methods used for estimating the magnitude of the contributions to formation/mixing entropies
- Models of value in the calculation of formation/ mixing entropies for real multi-component alloys and of value in the calculation of phase diagrams for multi-component, multi-phase systems
- The value of the cluster/site approximation for describing the configurational contributions in multi-component, multi-phase systems, and recent developments in its application
- Methods suitable for the estimation of the magnitude of other contributions to formation/mixing entropies

About the Speaker

W. Alan Oates is the Honorary Visiting Professor at the Institute for Materials at the University of Salford in the United Kingdom. A Fellow at the Institute of Metals, Mining and Materials in London since 1978, he earned his doctorate from The University of Newcastle in Australia. Oates' interests recently are in developing a higher order approximation which is suitable for multi-component alloys and in the thermodynamic modeling of intermetallic compounds.

Extraction & Processing Division Luncheon Lecture

"China's Growing Importance in the Metals Field With an Emphasis on Alloying Additions for the Aluminum Industry"

Albert Hayoun

Tuesday, March 14, Noon to 1:45 p.m.
Henry B. Gonzalez Convention Center
Ballroom C3, Level 3

Luncheon tickets may be purchased at the meeting registration desk.

by Albert Hayoun
President of Standard Resources Corporation

About the Topic

This presentation relates the history leading to China's ascendance to the important position it now holds in the metals market and traces its recent history as a supplier and consumer of alloying additions, such as silicon metal and magnesium metal, in the aluminum industry.

About the Speaker

Albert Hayoun is president of Standard Resources Corporation, a marketing firm specializing in metals, minerals and alloys. He assisted in establishing the company in 1994 and has helped develop relations with a number of mining and metallurgical companies in China. Hayoun has also established agencies, companies and subsidiaries in several countries including China, Mexico and Venezuela. His work over the past 33 years has involved importing and exporting castings, forgings, pig iron, ferro alloys, metals, minerals and alloys. He began his career in the metallurgical field in 1973 after receiving a bachelor's degree from Brooklyn College.

An Added Benefit for Nonmembers

Attendees registered in the Nonmember Author and Nonmember categories receive a one-year, complimentary associate membership to TMS for 2006!

As an associate member, you will have access to the technical information and professional network you need to advance your work:

- Free print and electronic subscription to *JOM*, a monthly technical journal covering varied subjects important to the minerals, metals and materials world
- Access to TMS E-Library, with online databases, engineering reference books and analytical tools, powered by Knovel
- Free subscription to *TMS Letters*, the online technical journal providing updates to cutting-edge research in a concise format.
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Your membership card and new member packet will be on their way to your mailbox following the annual meeting, but you may begin taking advantage of your membership once your annual meeting registration fee is received and processed.

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TMS

Your Professional Partner for Career Advancement

The Minerals, Metals & Materials Society (TMS) is the professional organization encompassing the entire range of materials in science and engineering, from minerals processing and primary metals production to basic research and the advanced applications of materials. The Society's broad technical focus covers light metals; electronic, magnetic and photonic materials; extraction and processing; structural materials; and materials processing and manufacturing.

Our Members

Included among TMS professional and student members are metallurgical and materials engineers, scientists, researchers, educators and administrators who work in industry, government and academia. They hail from more than 70 countries on six continents.

Our Mission

The mission of TMS is to promote the global science and engineering professions concerned with minerals, metals and materials. The Society works to accomplish its mission by providing technical learning and networking opportunities through interdisciplinary and specialty meetings; short courses; publications, including five journals and proceedings; and its Web site.

To learn more, visit www.tms.org.

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Technical Program

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San Antonio, Texas, USA

TECHNICAL PROGRAM

Henry B. Gonzalez Convention Center; San Antonio, Texas USA; March 12-16, 2006

MONDAY

2006 Nanomaterials: Materials and Processing for Functional Applications: Functional Applications of Nanoscale Materials

Sponsored by: The Minerals, Metals and Materials Society, TMS Electronic, Magnetic, and Photonic Materials Division, TMS: Nanomaterials Committee
Program Organizers: W. Jud Ready, GTRI-EOEML; Seung Hyuk Kang, Agere Systems

Monday AM Room: 214C
March 13, 2006 Location: Henry B. Gonzalez Convention Ctr.

Session Chairs: W. Jud Ready, GTRI-EOEML; Seung Hyuk Kang, Agere Systems

8:30 AM Introductory Comments

8:35 AM Invited
Oxide Nanobelts for Electromechanical Coupled Nanodevices: *Zhong Lin Wang*[1]; [1]Georgia Institute of Technology

Piezoelectricity is an important phenomenon that characterizes the electromechanically coupled response of a material, and it has widely been used in science and technology. At nano-scale, most of the studies have been carried out for exploring the semiconducting properties of quantum dots, nanowires as well as nanotubes, but the nano-scale piezoelectric property remains an unexplored field until recently. In our laboratory, we have synthesized a series of novel nanostructures of ZnO, a material that is semiconducting and piezoelectric. The piezoelectric coefficient of a piezoelectric nanobelt has been found to be almost tripled compared to the value of the bulk, clearly indicating the exciting applications of piezoelectric ZnO nanobelts for nano-scale electromechanical coupled sensors, transducers, switches and resonators. This talk will focus on our recent progress in investigating the growth, formation process, kinetics and potential applications of piezoelectric nanobelts, nanorings and nanohelixes.

9:00 AM Invited
Multifunctional Complex Oxide Heterostructures: *Ramamoorthy Ramesh*[1]; [1]University of California

Complex perovskite oxides exhibit a rich spectrum of functional responses, including magnetism, ferroelectricity, highly correlated electron behavior, superconductivity, etc. There exists a small set of materials which exhibit multiple order parameters; these are known as multiferroics.We are studying the role of thin film growth, heteroepitaxy and processing on the basic properties as well as magnitude of the coupling between the order parameters. A very exciting new development has been the discovery of the formation of spontaneously assembled nanostructures consisting of a ferromagnetic phase embedded in a ferroelectric matrix that exhibit very strong coupling between the two order parameters through 3-dimensional heteroepitaxy. This work is supported by the ONR under a MURI program.

9:25 AM Break

9:40 AM Invited
Control of Nanomaterials Geometry for Advanced Technical Applications: *Sungho Jin*[1]; [1]University of California, San Diego

The building block of nanotechnology is the nanomaterials. The fascination and great technical promises associated with nanoscale materials are based on the significant changes in their fundamental physical and chemical properties. For eventual engineering applications of nanomaterials, an ability to control not only their intrinsic structures and properties but also their basic geometry in terms of diameter, length, alignment, periodicity and spacing is essential. Synthesis of complex or advanced shapes and nanocomposites deviating from a simplistic circular or linear geometry is also useful for some applications. In this talk, some unique examples of controlling the geometry of nanomaterials such as carbon nanotubes, Ti-oxide nanotubes, magnetic nanoparticles, nanoislands, and other nanostructures will be described, and the implications of such geometry controls for potential electronic, chemical, mechanical and bio applications will be discussed.

10:05 AM Invited
The Performance of Carbon Nanotube Electron Sources: *Kenneth Teo*[1]; N. de Jonge[2]; E. Minoux[3]; L. Gangloff[1]; L. Hudanski[3]; O. Groening[4]; M. Allioux[2]; J. T. Ooostveen[2]; D. Dieumegard[3]; F. Peauger[3]; P. Legagneux[3]; W. I. Milne[1]; [1]University of Cambridge; [2]Philips Research Laboratories; [3]Thales Research and Technology; [4]Federal Laboratories for Materials Testing and Research

Multiwalled carbon nanotubes/fibers (CN) are pursued here as field emission electron sources because of their whisker-like shape, high aspect ratio, high conductivity, thermal stability and resistance to electromigration. Here, the key performance parameters for individual CN emitters and CN emitters which are arrayed are investigated, and the factors which affect these parameters studied. For individual CN emitters, results which show remarkably stable, low noise, and bright electron emission have been obtained. The emitter current fluctuation observed over 1 hr was merely 0.5% and the emitter noise can be fitted to 1/f behavior over a bandwidth of 0.1 –25 Hz, above which, random shot noise was observed to dominate over the emitter noise. The noise percentage was determined to be 0.08% +/- 0.06% (ie. signal to noise ratio of 761-5000) various CNT emitters operated at several current levels. The single CNT emitter was also brighter than tungsten cold emitters or Schottky.

10:30 AM Invited
Growth of Y-Junction Single-Wall Carbon Nanotube and Its Application: *Wonbong Choi*[1]; [1]Florida International University

The Y-junction single-wall carbon nanotubes (SWNTs) have attracted much attention due to their potential to be used as future nano electronics, where the third terminal is used for controlling the switching, power gain, or other transiting purposes. We synthesized Y-junction SWNTs using controlled catalysts by chemical vapor deposition. Transmission electron microscopy confirmed the formation of Y-junction SWNTs with diameters of 2 – 5 nm. Radial breathing mode peaks of Raman show that our sample has both metallic and semiconducting, indicating the possible formation of Y-branching with different electrical properties. The electrical transport properties across Y-SWNTs show rectifying behavior and exhibit ambipolar at room temperature. Gating operation shows the subthreshold swing of 0.7~ 1V/decade and Ion/off ratio of 10^4~10^5 with off-state leakage current ~10^-13A. Surface modified Y-junction SWNT indicates its potential application as sensor. The further enzyme catalyst modification is employed to sense specific biological analysts through electrochemical technique.

10:55 AM Break

11:10 AM Invited
Novel Electrical Phenomena in Carbon Nanotube Y-Junctions: *Prabhakar Bandaru*[1]; Chiara Daraio[1]; Sungho Jin[1]; Apparao Rao[2]; [1]University of California, San Diego; [2]Clemson University

Novel nano-engineered Carbon Nanotube (CNT) morphologies such as Y- and T-junctions have been predicted to have new functionalities and herald a new generation of nano-electronic components. These non-linear CNT forms have a natural asymmetry at the junction due to the presence of non-hexagonal defects, required for energy minimization. The carrier delocalization and the inevitable presence of catalyst particles, introduced during synthesis, at the bends induce a net charge and scattering which can be exploited for electronics. I will discuss the structure-electrical prop-

erty correlations in one particular form- the Y-junction. I will show evidence for novel electrical behavior, such as an abrupt modulation of the current from an on- to an off- state, presumably mediated by defects or the topology of the junction. The mutual interaction of the electron currents in the three branches of the Y-junction is shown to be the basis for a potentially new logic device.

11:35 AM Invited
Fabrication and Performance of Novel Carbon Nanotube-Based Biofuel Cell and Biosensor: Yubing Wang[1]; *Zafar Iqbal*[1]; [1]New Jersey Institute of Technology

We have grown thin films of vertically aligned single wall carbon nanotubes (SWNTs) on doped silicon wafers using a chemical vapor deposition (CVD) process with ethanol as carbon source and densely deposited bimetallic cobalt/molybdenum as catalyst. Glucose oxidase (GOx) and bilirubin oxidase (BOD) enzymes dissolved in a buffer were reacted with the nanotube tips by our recently developed rapid microwave process[1] and also by electrochemical reaction. A non-compartmentalized glucose/air biofuel cell with SWNT/GOx as anode and SWNT/BOD as cathode in an electrolyte comprised of 100 mM ß-D-glucose in pH 7 phosphate buffer, was assembled. The performance characteristics of the biofuel cell and that of a glucose biosensor consisting of a SWNT/GOx sensing electrode and a platinum electrode in a similar electrolyte, will be discussed. [1]Y. Wang, Z. Iqbal and S. Mitra, J. Amer. Chem. Soc. – to be published.

12:00 PM Invited
Long Carbon Nanotubes and Nanotube Cotton by Chemical Vapour Deposition: *Yuntian T. Zhu*[1]; Lianxi Zheng[1]; Michael J. O'Connell[1]; Steve K. Doorn[1]; [1]Los Alamos National Laboratory

In this talk we report the synthesis of long carbon nanotubes and carbon nanotube cotton by catalytic chemical-vapour-deposition. Both were grown on Si substrates. SEM images following a single nanotube revealed its length as 40 mm, which is a world record. Atomic force microscopy and Raman spectrum were performed, indicating that carbon nanotubes are single walled with diameter range of 1nm~2.25nm. The evolution of surface morphology according to growth conditions was also studied using scanning electronic microscopy. Growth and termination mechanism will be discussed. The carbon nanotube cotton is made of puffy, tangled long multi-wall nanotubes, resembling cotton and individual cotton fibers. The nanotube cotton can be easily spun into nanotube fibers. These long nanotubes and nanotube cotton may have functional applications such as nano electric wires and scaffolding for neuronal growth.

3-Dimensional Materials Science: Microstructure Representation

Sponsored by: The Minerals, Metals and Materials Society, TMS Structural Materials Division, TMS: Advanced Characterization, Testing, and Simulation Committee
Program Organizers: Jeff P. Simmons, U.S. Air Force; Michael D. Uchic, Air Force Research Laboratory; Dorte Juul Jensen, Riso National Laboratory; David N. Seidman, Northwestern University; Anthony D. Rollett, Carnegie Mellon University

Monday AM — Room: 205
March 13, 2006 — Location: Henry B. Gonzalez Convention Ctr.

Session Chairs: P. W. Voorhees, Northwestern University; Craig S. Hartley, El Arroyo Enterprises LLC

8:30 AM Introductory Comments

8:35 AM Invited
Three-Dimensional Microstructural Residual-Stress Response Isosurfaces: *Edwin R. Fuller*[1]; Thomas Wanner[2]; David M. Saylor[3]; [1]National Institute of Standards and Technology; [2]George Mason University; [3]Food and Drug Administration

When a polycrystalline material with crystalline thermal expansion anisotropy is cooled (or heated), residual stresses develop within the microstructure. These stresses develop into a network structure with a length scale that encompasses many grains. The size of the network structure depends strongly upon the intergranular misorientation distribution function, but is also influenced by the grain orientation distribution function. This phenomenon, while readily apparent in two-dimensional, microstructure-based finite-element simulations, is not so clear in similar three-dimensional simulations. To elucidate the microstructure-induced response, response isosurfaces are generated by defining surfaces at a specific threshold level of residual-stress response. The resulting distribution of residual stresses throughout the microstructure is considered as a geometric object itself: a microstructure response isosurface. Computational homology invariants (e.g., Betti numbers) are used to characterize and quantify these residual-stress response isosurfaces.

9:00 AM
The Three-Dimensional Microstructure of Materials: D. Kammer[1]; J. Wilson[1]; *P. W. Voorhees*[1]; S. A. Barnett[1]; R. Mendoza[1]; [1]Northwestern University

Recent advances in computational and experimental techniques now allows for the routine visualization of the three-dimensional microstructure of materials. This opens new routes to explore the relationship between materials processing and structure. Examples of three-dimensional reconstructions of microstructure in systems ranging from solid oxide fuel cells to dendritic solid-liquid mixtures will be given. Using this three-dimensional information it is possible to quantify the morphology of complex 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 via measurements of the normals to the interfaces, and the genus of the microstructure. We will also discuss the measurement of the triple junction line length in solid oxide fuel cells, a crucial input to understanding the electrochemical performance of these cells.

9:20 AM
Characterizing 3D Microstructure Using the Minkowski Functionals: *James Steele*[1]; [1]Steele Works

3D microstructural patterns can be globally quantified by the set of valuations (parameters) known as the Minkowski Functionals. These patterns represent 3D spatial arrangements of thermodynamic phases as embedded within E3. The four parameters, which constitute the Minkowski Functionals are; volume, V(X), surface area, S(X), integral mean curvature, M(X), and integral Gaussian curvature, K(X), for a 3D object X. These four parameters form a complete set of global descriptors for 3D microstructure when estimated as volume densities. This is a result of the famous characterization theorem of Hadwiger (1957), which shows that the four parameters, {Vv, Sv, Mv, Kv} form a complete set of global descriptors among those that are kinematically invariant. Stereological methods for estimating volume densities of the Minkowski Functionals will be described. Examples of measurements of the Minkowski Functionals for characterizing dendrites, porosity in sandstone, and bi-continuous "sponge-like" copolymers will be discussed.

9:40 AM
Correlations in Three-Dimensional Evolving Microstructures: *Ke-Gang Wang*[1]; Martin Glicksman[1]; [1]Rensselaer Polytechnic Institute

We will discuss our recent modeling efforts to study quantitatively the evolution of spatial and temporal correlations in aging phase mixtures. Large-scale simulations will be shown of three-dimensional microstructures evolving via diffusion-mediated multiparticle diffusion. Spatial correlations developed in such microstructures are revealed via simulation, along with associated stochastic phenomena that occur during aging. Measured pair distribution functions will be shown. Mean inter-particle spacing is characterized in our study as a function of aging time through the distribution of spacings between pairs of phase domains, and through the distribution of nearest-neighbor distances. Characterizing local features developed in a two-phase microstructure employing statistical measures permits demonstrating their influence on the properties of the material. Finally, theoretical and computational results from this study will be compared with experimental observations on two-phase alloys.

10:00 AM
Percolation Theory for Two-Phase Materials with Nonrandom Topologies: *Megan E. Frary*[1]; Christopher A. Schuh[1]; [1]Massachusetts Insti-

tute of Technology

Percolation theory is commonly used to develop microstructure-property relationships for two-phase materials. Although many composite microstructures have engineered spatial correlations among the constituent phases, percolation-based models often assume random arrangement of the phases. Using 3-D microstructure simulations, we systematically study topologically-varied two-phase microstructures with different states of ordering or segregation. We find that the topological state of the microstructure strongly affects percolation behavior and that the percolation threshold changes by as much as ±0.20 when local correlations are introduced. In order to quantify these effects, we propose that all microstructures be mapped into a "correlation-space", upon which percolation behavior is easily superimposed. In this way the correlation-dependence of properties such as the percolation threshold, connectivity length and mean cluster size of the microstructure can be easily predicted.

10:20 AM Break

10:40 AM

Reconstructing 3D Microstructures: A Comparison between Simulated Annealing and Evolutionary Algorithm Methods: David Basanta[1]; Elizabeth A. Holm[2]; Peter Bentley[3]; *Mark Miodownik*[1]; [1]King's College London; [2]Sandia National Laboratories; [3]University College London

We have investigated two computational methods to reconstruct 3D microstructures from 2D inputs. The first method is a simulated annealing approach based on voxel swapping pioneered by Torquato et al.[1] and the second method is a genetic algorithm approach based on developmental evolutionary algorithm MicroConstructor[1]. We take a range of morphologically different 2D input microstructures and use both methods to reconstruct 3D microstructures which have the same stereological parameters. We find that each method performs better than the other on different types of input structure, but that in general the genetic algorithm outperforms the simulated annealing as the system size increases. [1]Yeong, C.L.Y. and Torquato, S. Reconstructing random media. II. Three-dimensional media from two-dimensional cuts. Physical Review E. 58:224-233 (1998). [2]Basanta D., Miodownik M.A., Holm E.A., and Bentley P.J. Evolving 3D Microstructures from 2D Micrographs using a Genetic Algorithm. Met Trans A. 36A:1643-1652. (2005).

11:00 AM

A Simulated Annealing Monte Carlo Approach to the Reconstruction of Two-Phase Microstructures: *Marc J. DeGraef*[1]; Jeremiah P. MacSleyne[1]; [1]Carnegie Mellon University

The microstructural description of Ni-base superalloys requires the use of two-point correlation functions and lineal path functions. After these functions have been obtained from experimental observations, such as focused ion beam serial sectioning, they may be used to generate new microstructures that are similar to the input microstructures in the statistical sense. In other words, anisotropic 1- and 2-point correlation functions and other higher order characterizations are similar to data compression schemes, where the original digital microstructures are distilled to a few quantities. These few quantities or characterizations, whenever necessary, can be "decompressed" back to an ensemble of digital microstructure images (with some unavoidable loss of detail). We will illustrate this reconstruction by means of a simulated annealing Monte Carlo approach. We will discuss the use of 2-point correlation functions along specific directions relative to the microstructure, as well as the use of the full 3D 2-point correlation function.

11:20 AM

Simulation Models to Generate Realistic Microstructures of Discontinuously Reinforced Aluminum Alloy (DRA) Composites Using Real Particle Morphologies: *Harpreet Singh*[1]; Arun Gokhale[1]; [1]Georgia Institute of Technology

Computer models have been used to simulate microstructures of DRA composites. This novel technique can generate realistic microstructures by combining the use of real particle morphologies/shapes with non-uniform (clustered) spatial arrangement as observed in the real microstructures. Both short-range and long range order of real microstructures has been captured in the simulations by generating sufficiently large microstrucrual windows containing over ten thousand particles at high resolution. Simulated microstructures were then statistically compared to the real ones using two-point correlation functions and were shown to match closely up to 500 micron length.

11:40 AM

Automated Microstructural Feature Representation Using Principal Component Analysis and Classification Techniques: *Jeff P. Simmons*[1]; Dennis M. Dimiduk[1]; Marc J. DeGraef[2]; [1]U.S. Air Force; [2]Carnegie Mellon University

Fusing computer and experimental techniques, along with a proliferation of simulation techniques, creates opportunities for generating massive collections of statistically significant microstructural data. Taking full advantage of these opportunities requires accelerating the data analysis rate and developing an ability to use the data for solving multiple problems. The human resources available for analysis will likely decrease for the foreseeable future, requiring the development of optimal representations of data to be automated to keep pace with its generation. Utilizing this information will require that representations be standardized without discarding information simply because it does not appear to be relevant to the issues that motivated its generation. Towards these ends, a framework for representing particle and particle neighborhood information in microstructures has been developed that automates sample selection, representation, and classification into typical/rare event classes. It is expected that these basic stochastic building blocks will enable development of automated representations of microstructures.

12:00 PM

An Information-Theoretic Approach for Obtaining Property PDFs from Macro-Specifications of Microstructural Variability: *Nicholas Zabaras*[1]; Veera Sundararaghavan[1]; Sethuraman Sankaran[1]; [1]Cornell University

Probability distribution functions (PDFs) providing a complete representation of property variability in polycrystalline materials are difficult to obtain. Reconstruction of probability distribution of material properties on the basis of limited morphological information is an inverse problem of practical significance since many macroscopic properties depend strongly on geometrical variability of the micro-constituents. We characterize the unknown probabilities of the microstructural parameters making use of the macro-information given in the form of average values (such as average grain sizes) and using the concepts of maximum information entropy (MAXENT) and stochastic geometry. The PDFs are used to generate consistent samples of microstructures whose properties are assessed using a multi-scale framework based on a newly developed fully implicit Lagrangian large strain homogenization framework.

Advanced Materials for Energy Conversion III: A Symposium in Honor of Drs. Gary Sandrock, Louis Schlapbach, and Seijirau Suda: Plenary Session

Sponsored by: The Minerals, Metals and Materials Society, TMS Light Metals Division, TMS: Reactive Metals Committee
Program Organizers: Dhanesh Chandra, University of Nevada; John J. Petrovic, Petrovic and Associates; Renato G. Bautista, University of Nevada; M. Ashraf Imam, Naval Research Laboratory

Monday AM	Room: 214B
March 13, 2006	Location: Henry B. Gonzalez Convention Ctr.

Session Chairs: Sunita Satyapal, U.S. Department of Energy; Scott Jorgensen, General Motors; Farshad Bavarian, Chevron Texaco Technology Ventures LLC

8:30 AM Introduction to the Symposium by Chandra, Petrovic, Bautista and Imam

8:45 AM Presentation of Plaques and Comments by Gary Sandrock

8:55 AM Presentation of Plaques and Comments by Luis Schlapbach

9:05 AM Presentation of Plaques and Comments by Seijirau Suda

9:15 AM Plenary
The Challenge of Vehicular Hydrogen Storage: Grace Ordaz[1]; John J. Petrovic[2]; Carole Read[1]; *Sunita Satyapal*[1]; George Thomas[3]; [1]U.S. Department of Energy; [2]Los Alamos National Laboratory; [3]Sandia National Laboratories

Hydrogen is a potential energy carrier for vehicular applications. However, hydrogen-powered vehicles require a driving range of greater than 300 miles in order to meet customer needs and effectively compete with other technologies. For the overall vehicular fleet, this dictates that a range of 5-13 kg of hydrogen be stored on-board, within stringent weight, volume, and system cost constraints. Vehicular hydrogen storage thus constitutes a major scientific and technological challenge. To meet this challenge, the DOE's National Hydrogen Storage Project has been initiated which focuses on materials-based technologies. Centers of Excellence in metal hydrides, chemical hydrides, and carbon-based materials have been established, as well as independent university and industry projects in the areas of new concepts/materials, hydrogen storage testing, and storage system analysis. Recent technical progress in each of these areas will be presented as well as collaborative hydrogen storage activities under the International Partnership for the Hydrogen Economy (IPHE).

9:40 AM Plenary
Gary Sandrock and Metal Hydrides: *James J. Reilly*[1]; [1]Brookhaven National Laboratory

Certainly it would be impossible to give an historical perspective of metal hydride energy storage compounds and their current status without recording the contributions of Gary Sandrock. Gary received his Ph.D. in metallurgy from Case Western Reserve University in 1971 and was employed by INCO in the same year. In 1974 turned his research interests towards rechargeable AB and AB5 metal hydrides. This lecture will take us from that point to the present time. It will be noted that Gary was involved in almost every novel aspect of the field over a thirty year period; low temperature, low capacity intermetallic compounds for H storage; Ni/MH batteries and the high capacity alanates and alanes of current interest. In addition he currently serves as the U.S. Operating Agent (Task 12) to the IEA.

10:05 AM Break

10:20 AM Plenary
Sodium Borohydride as the Hydrogen and Protide Source: *Seijiau (Seiji) Suda*[1]; Zhou-Peng Li[1]; Yang-Mng Sun[1]; Bing-Hong Liu[1]; Nobuto Morigasaki[1]; Singo Hara[1]; [1]Materials and Energy Research Institute Tokyo, Ltd.

Sodium borohydride (SBH: NaBH4) can be regarded as one of the most practical H-storage material today. It contains 10.6mass% of hydrogen, which is available under ambient conditions as the safe source of gaseous hydrogen (H2) by catalytic hydrolysis for PEMFC and protide (H-) by applying directly as the aqueous solution for DBFC (Direct Borohydride Fuel Cell). As SBH is used as the form of aqueous solution in either application, the practical H-capacity is considerably reduced to 3 to 6wt% because of the solubility limits and the formation of crystalline materials. The SBH solution forms condensed sodium metaborate (SMB: NaBO2•4H2O) solution as "spent fuel" and it may cause several technical issues. Current SBH production process is definitely unaffordable in the future H-storage applications and SMB must be recyclable and regerative to produce SBH from the waste-treatment of "B" H-containing materials and cost-reduction viewpoints.

10:45 AM Plenary
Important Events in the Recent Past and Near Future of Hydrogen Storage for Mobile Applications: *Scott Jorgensen*[1]; [1]General Motors

Hydrogen storage research has a long history, with a recent surge of new materials and new concepts. Important progress has occurred in the area of solid phase materials for storage, tank materials and engineering, and new types of materials. More importantly, an understanding of these materials is beginning to allow prediction of hydrides with improved properties. The performance of these new hydrogen storage systems begins to approach that of physical containment methods. The next step is to directly target performance that will permit commercialization.

11:10 AM Keynote
Activated MgH2 Powders: Principles of D-Metal Activation Process, Mass Production at Factory Scale, Design and Numerical Simulation of a Tutorial Tank: *Daniel Fruchart*[1]; Jean Charbonnier[1]; Patricia de Rango[1]; Michel Jehan[2]; Philippe Marty[3]; Salvatore Miraglia[1]; Sophie Rivoirard[1]; Nataliya Skryabina[4]; [1]Centre National de la Recherche Scientifique; [2]MCP Technologies; [3]LEGI-GRETH; [4]Perm State University

The main principles of activation process with d-metal additions to magnesium powder for fast absorption and desorption kinetics have been evaluated from X-ray diffractometry, in-situ neutron diffraction experiments, as well as from kinetics and PCT measurements. More than 6 w% reversible hydrogen mass can be stored reversibly and the reaction kinetic was found quite fast even at rather low temperature. Production of such activated powders at a pilot scale in a factory has been made effective by using a two step route with a dedicated autoclave for the production of a primary hydride and then the delivery of kg batches of ball-milled MgH2 using metal catalysts. Furthermore, we have developed a small size but well equipped with many sensors MgH2 tank to monitor the gas, heat and cooling flows for time optimized charge/discharge. This experimental operations are analyzed parallel using a specific 2D code for numerical simulation.

11:35 AM Invited
Novel and Safe Sodium Borohydride Based Fuel: *Menachem Givon*[1]; Jonathan Goldstein[1]; [1]HyoGen Ltd

Sodium borohydride is a good hydrogen carrier for chemical hydride based vehicle systems (the hydrogen content of this material alone is above 10wt%), and borohydrides may well become an important part of a future "Hydrogen Economy". However, sodium borohydride aqueous solutions in use today for hydrogen generation are corrosive and not fully stable, especially at high ambients. In addition, the by-product of hydrogen generation, sodium metaborate, has poor solubility in water and tends to solidify and block pipes, pumps and valves. As a result, systems based on aqueous borohydride only achieve about 4wt% hydrogen storage fraction. A new approach is described, based on encapsulated solid borohydride in a non-aqueous carrier fluid, in which the sodium metaborate by-product is processed, pelletized and stored onboard prior to refueling as a pumpable slurry. This approach leads to practical hydrogen storage fractions of over 7wt% on a systems basis.

Aluminum Reduction Technology: Environmental Elements

Sponsored by: The Minerals, Metals and Materials Society, TMS Light Metals Division, TMS: Aluminum Committee
Program Organizers: Stephen Joseph Lindsay, Alcoa Inc; Tor Bjarne Pedersen, Elkem Aluminium ANS; Travis J. Galloway, Century Aluminum Company

Monday AM — Room: 7A
March 13, 2006 — Location: Henry B. Gonzalez Convention Ctr.

Session Chair: Paul G. Campbell, Alcoa Inc

8:30 AM
Soderberg Technology – A Challenge or an Opportunity: *Viktor Mann*[1]; [1]RUSAL

One of the key objectives shared by aluminum producers worldwide is to reduce the environmental impact of aluminum production. RUSAL, jointly with some of the world's leading aluminum producers using the Soderberg technology, is undertaking a research program to reduce the environmental impact through modernizing Soderberg cells, installing additional scrubbers, as well as seeking ways to improve technological processes. RUSAL's Engineering and Technology Center is leading the company's effort to reduce volatile hydrocarbon emission levels (bringing them in line with the OsPar Convention recommendations), lower anode mix consumption factor per 1 tone of aluminum by 5-8%, and raise current density to the unparalleled figure of 0.82-0.85 A/sq. cm. (190-210

kA). The new Soderberg or the so-called "colloid anode" technology, is being developed through an upgrade approach that allows introduction of new technology with reasonable investment, making it highly competitive economically and viable environmentally.

9:00 AM

Methods for Calculating PFC Emissions from Primary Aluminium Production: *Jerry Marks*[1]; [1]International Aluminium Institute

Accurate calculation of PFC emissions are of increasing importance for primary aluminium producers because of the adoption of the Kyoto Protocol by a number of countries and because a number of other companies have entered into formal agreements with their national governments to reduce greenhouse gas (GHG) emissions. The methods for calculating PFC emissions rates per tonne of aluminum produced have not been updated since 2000. The Intergovernmental Panel on Climate Change (IPCC) is in the process of developing revised Good Practice Guidelines that will result in a number of changes in current methodology. This paper describes the background for these changes, the proposed new equations and the impact of these changes on emissions of PFCs.

9:30 AM

Root Causes of Variability Impacting Short Term In-Plant PFC Measurements: Neal R. Dando[1]; *Weizong Xu*[1]; Lise Sylvain[1]; [1]Alcoa Inc

The perfluorocarbon gases tetrafluoromethane (CF4) and hexafluoroethane (C2F6) are known greenhouse gases that are emitted from aluminum smelters during transient conditions known as anode effects. Alcoa has voluntarily monitored PFC emissions from aluminum for over 10 years under a voluntary agreement known as the Voluntary Aluminum Industrial Partnership with the US Environmental Protection Agency. The purpose of these relatively short duration (2-3 day) PFC studies was to generate technology-specific "slope" terms that could be used to calculate future PFC emissions from aluminum smelters. In the present effort, PFC emissions were monitored for one-month durations at both pre-bake and Soderberg smelters in order to collect data on significant populations of anode effects of varying duration and kill strategy. The purpose of this study was to identify and characterize the process-based root causes of variability observed in short term studies of PFC emissions.

10:00 AM Break

10:15 AM

Reduction of HF Emissions from the TRIMET Aluminum Smelter Optimizing Dry Scrubber Operations and Its Impact on Process Operations: *Martin Iffert*[1]; Markus Kuenkel[1]; Maria Skyllas-Kazacos[2]; Barry Welch[2]; [1]Trimet Aluminium AG; [2]University of New South Wales

Aluminum smelters worldwide are challenged by increasing ecological and economical pressure. Higher line amperages gain production output but increase the HF load on dry scrubbers. Another important factor today is the tight alumina market, hence it is necessary to accomodate dry scrubber and potline operations to different alumina sources and qualities regarding their HF generation and scrubbing efficiency as well as its impact on bath chemistry. The TRIMET smelter optimised dry scrubber operations by the use of a laser based HF measuring system in each of the 20 filter modules. Based on the HF level in the outlet of each filter the alumina flow to each filter is pulse-duration modulated, thus tightly control the HF emission level in the outlet gas. This paper describes the application of the new measuring and control principle and its impact on HF scrubbing efficiency and bath chemistry.

10:40 AM

Impact of Pot Cover Integrity on HF Emission and Evolution: *Neal R. Dando*[1]; Robert Tang[1]; [1]Alcoa Inc

Aluminum electrolysis pots evolve gaseous fluoride (HF) owing to hydrolysis of the molten salt bath. The fluoride that enters the fume treatment system is considered evolution, while that which does not enter or escapes the fume treatment system is considered emission. A range of smelter-owned factors such as pot chemistry, operating practice, pot tending practice and ore feeding affect the dynamics of HF evolution from smelting cells. Issues such as hooding efficiency, hooding flow rates and crust cover integrity are primary factors impacting HF emissions from the pots. Real-time HF evolution and emission monitoring was performed on individual operating smelting pots to generate quantitative measurements of evolved fluoride as a function of crust cover condition. The purpose of this effort was to gain a better understanding of the relationship between fluoride evolution and emission as impacted by pot tending practices.

11:05 AM

Correlation of Fluoride Evolution with on Line Gas Duct Temperature: *Nilton Freixo Nagem*[1]; Eliezer S. Batista[1]; Ari F. Silva[1]; Valerio Gomes[1]; Haroldo Ferreira[1]; Raimundo R. S. Mendes[1]; [1]Consórico de Alumínio do Maranhão - ALUMAR

A global strategy to reduce all emissions sources is in action. Continuous improvement and sustainable development are the driving forces to seek new ways to reduce and control fluoride emissions. The fluoride generation is mainly produced by smelting activity; it forms by the reaction of a source of hydrogen (moisture, H ion) and molten or volatilized cryolitic bath. Literature shows the impact of operation activities on fugitive fluoride emission. This work shows an on line duct temperature measurements of the pot gas and correlate with fluoride emissions (using an open pass tunable diode laser). The conclusion demonstrates the correlations with the operations activities, process parameters with fluoride emission. Finally, this paper shows that the pot duct temperature can be an important process parameter to control and minimize the fugitive fluoride. This system is able to monitor pot conditions and operational activities based on temperature variation of the pot gas.

11:30 AM

New Design of Cover for Anode Trays: *Jean-Pierre Gagne*[1]; Robin Boulianne[1]; Jean-François Magnan[1]; Marc-André Thibault[1]; Gilles Dufour[2]; Claude Gauthier[2]; [1]STAS; [2]Alcoa

During the production of aluminium in smelters, the anodes used in electrolysis cells have to be replaced frequently. Anode butts are usually disposed on anode trays for transportation and cooling, a practice where Hydrogen Fluoride (HF) is emitted in large quantities. In 2001, special lids developed by Alcoa Deschambault to fit on the anodes trays close and open according to the anode movements, with the result of significant reductions of HF emissions. However, they are expensive to maintain and require short life consumable parts.In January 2004, STAS and Alcoa decided to develop a more efficient design of lid, with lower maintenance costs and no need of consumable material (like red silicone cushions). This paper presents a summary of the work performed to obtain the new design as well as a summary of the test results.

11:55 AM

Running Results of the SPL Detoxifying Pilot Plant in CHALCO: Wangxing Li[1]; *Xiping Chen*[1]; [1]Chalco

A new process to detoxify SPL had been developed in Chalco in December 2003, and the first SPL detoxifying pilot plant of China had been established in Chalco by the end of 2004. During the past five months of 2005, the pilot plant has been put into running. Till the end of May 2005, 104 tons SPL have been detoxified, and 119 tons innoxious SPL solid residue have been received for processing. The average soluble F—and CN—in the solid residue are respectively 39.7mg/l and 0.053mg/l, which are lower than China national permitted discharge standard 50.0mg/l and 1.0mg/l, the final product is benign. Now the pilot plant is working well, and experiments on how to make use of the benign SPL solid residue are processing.

12:20 PM End

Aluminum Reduction Technology: Inert Anodes - Part I

Sponsored by: The Minerals, Metals and Materials Society, TMS Light Metals Division, TMS: Aluminum Committee
Program Organizers: Stephen Joseph Lindsay, Alcoa Inc; Tor Bjarne Pedersen, Elkem Aluminium ANS; Travis J. Galloway, Century Aluminum Company

Monday AM Room: 7B
March 13, 2006 Location: Henry B. Gonzalez Convention Ctr.

Session Chair: Geoffrey Paul Bearne, Comalco Ltd

8:30 AM
Anodic Overvoltage on Metallic Inert Anodes in Low-Melting Bath: *Jomar Thonstad*[1]; Adolf Kisza[2]; Jan Hives[3]; [1]Norwegian University of Science and Technology; [2]University of Wroclaw; [3]Slovak Technical University

For inert anodes the standard emf is about one volt higher than for carbon anodes, and it is then important that the anodic overvoltage is as low as possible in order to save energy. An overview of existing literature will be given. In the experimental work inert anodes made of a Cu-Ni-Fe alloy, with the composition 40 Cu-30 Ni-30 Fe (wt%), were tested in a low-melting electrolyte at 750°C with the composition 55 mol% NaF and 45 mol% AlF3, containing about 10 wt% excess alumina (weighed-in 13 wt%). Anodic overvoltage data were derived from impedance measurements. In unstirred melts it was observed that the Tafel lines bent upwards at quite low current densities, indicating diffusion limitations. In stirred melts straight Tafel lines were obtained, the overvoltage at 1 A/cm2 being of the order of 0.4 V. The diffusion coefficient of the electroactive species (dissolved alumina) was 2.23.10-5 cm2/s.

8:55 AM
Gas Evolution on Graphite and Oxygen-Evolving Anodes during Aluminium Electrolysis: *Torstein Utigard*[1]; Laurent Cassayre[2]; Gabriel Plascencia[3]; Tanai Marin[4]; Sharon Fang[1]; [1]University of Toronto; [2]Institute of Transuranium Elements; [3]CIITEC – IPN; [4]University of Chile

Anode gas evolution, growth and flow behaviour during aluminium electrolysis have been investigated using various experimental techniques, including water modelling, X-ray visualization and direct observation. Video recordings of oxygen-evolving anodes (SnO2, Cu, Cu-Ni, Cu-Al) and carbon anodes were performed in laboratory electrolysis cells of various scales. The water model also investigated the effects of slotted anodes on the gas escape from beneath large anodes. Beneath large horizontal anodes individual bubbles form and are then subsequently swept away by large sweeping bubbles flowing rapidly beneath the bottom surface. The gas behaviour on oxygen evolving anodes was very different from that with carbon with the formation of very small bubbles that released very quickly from the anode due to improved wetting of the anode by the electrolyte.

9:20 AM
The Oxygen-Evolving Metallic Anode for Aluminum Reduction Cells: *Thinh Nguyen*[1]; Vittorio De Nora[1]; Rene Von Kaenel[1]; [1]MOLTECH SA

The new nickel-doped cobalt oxide coating greatly improves the performance of the oxygen-evolving metal anode. The active coating is obtained by the oxidation of the Co-Ni alloy coating electroplated onto the surface of the anode. The dense and stable structure of the active coating constitutes a physical barrier against gaseous AlF3 and O2. Corrosion of the alloy substrate by fluoridation is suppressed, and its stationary oxidation rate under anodic polarization is very low. The experimental oxygen potential on the Co(Ni)O-coated metal anode has been measured. Analyses of the chemical environment and the temperature above the melt-line induced the development of a stem with a steel core protected by a copper oxide envelope. The structural stability of the stem under attack by HF at high temperature has been proved by testing under industrial conditions. The metallic anode-stem system has been tested successfully in cells at currents up to 30 kA.

9:45 AM
Modeling of a 30 kA Metallic Anode Test Cell: *Jacques Antille*[1]; Laurent Klinger[1]; Thinh Nguyen[2]; Vittorio De Nora[2]; [1]KAN-NAK SA; [2]MOLTECH SA

A 30 kA oxygen-evolving metallic anode test cell is modeled mathematically to predict the energy consumption and thermal balance under given operating conditions. The model is then used to find the optimal anode-to-cathode distance and the critical anode current densities for an improved design. The model predictions are validated by measurements on the 30 kA test cell.

10:10 AM Break

10:20 AM
Technical and Economical Evaluation of the Oxygen Evolving Metallic Anode in Aluminum Reduction Cells: *Rene Von Kaenel*[1]; Vittorio De Nora[1]; Thinh Nguyen[1]; [1]MOLTECH SA

A cell with metallic anodes could have a higher energy consumption than the conventional cell because the oxygen-evolving reaction has a higher thermodynamic potential than those at the conventional anode, while being less exothermal. As in conventional cells, good thermal balance is essential to ensure protection of the cell structure with a side ledge. To ensure thermal balance and minimise energy consumption, cells with metallic anodes must operate at a high current level, by maximising the anode current density and the active surface area. In commercial cells, two practical factors limiting the current density are the anode to cathode distance and the anode current density. An economic evaluation of the metallic anode is presented, for retrofitting a conventional cell and for a new design in a non-horizontal configuration. Production cost savings and further developments direction are discussed. A significant competitive advantage is achieved by using metallic anodes.

10:45 AM
Electrochemical Behavior of Metals and Binary Alloys in Cryolite-Alumina Melts: G. A. Tsirlina[1]; E. V. Antipov[1]; A. Yu. Filatov[1]; V. V. Ivanov[2]; *S. M. Kazakov*[1]; P. M. Mazin[1]; V. M. Mazin[1]; V. I. Shtanov[1]; Yu. A. Velikodny[1]; D. A. Simakov[2]; S. Yu. Vassiliev[1]; [1]Moscow State University; [2]Engineering and Technological Centre, Ltd.

Electrochemistry of Ni, Fe, and Cu metals as well as of their binaryalloys (including alloys with Al) is reported. To determine the characteristic potential regions of certain redox processes in cryolite-alumina melts, cyclic voltammetry, chronopotentiometry, and preparative potentiostatic electrolysis of Fe(III) and Cu(II) oxides dissolved in the melt are applied. The nature of electrolysis products and thin oxide films formed under open circuit and in the course of anodic polarisation is clarified by means of X-ray diffractometry and EDX analysis. Finally, some general trends of selective dissolution and oxidation for binary systems are formulated in the context of predicting the role of each component in the multicomponent alloys tested as the future inert anodes.

11:10 AM
Electrical Conductivity of Low Melting Cryolite Melts: *Olga Tkatcheva*[1]; Alexander Redkin[1]; Yurii Zaikov[1]; Vladimir Khokhlov[1]; Alexei Apisarov[1]; Vasylii Kryukovsky[2]; Anton Frolov[3]; [1]Institute of High Temperature Electrochemistry; [2]Russian Aluminum Company RUSAL; [3]Engineering-Technological Center Ltd, RUSAL

The modern industrial aluminum electrolysis is carried out at high temperature that leads to great energy consumption and fast corrosion of the construction materials. This situation can be improved by using low melting electrolytes such as KF-AlF3 (CR=1,3) with melting temperature below 600°C. The most important in this case is the value of electrical conductivity because it decreases with temperature very fast. The electrical conductivity of molten system KF-AlF3 (CR=1,3) has been measured in 680-770°C temperature range in capillary cell by impedance method. The electrical conductivity temperature dependence in molten systems KF-AlF3 –Al2O3 (CR=1,3), KF-AlF3–LiF (CR=1,3), KF-AlF3 –Al2O3-LiF (CR=1,3) have been measured in Egear type cell. The Al2O3 concentration was varied from 0 to 4,8 wt.% and the LiF concentration was changed from 0 to 10 wt.%. The results obtained show the possibility of usage of this electrolyte for industrial electrolyses.

11:35 AM

Study on the Nickel Ferrate Spinel Inert Anode for Aluminum Electrolysis: *Yihan Liu*[1]; Guangchun Yao[1]; Hongjie Luo[1]; Xiaoming Zhang[1]; [1]Northeastern University

In the late decades, a series of new technologies such as inert anode, wettable cathode and lower temperature electrolysis for primary aluminum production had been studied, for saving energy, debasing cost and erasing environment pollution. The thesis studied the preparation and the properties of cermet inert anode based on NiFe2O4 spinel. We choose the Ni2O3 and Fe2O3 as primary ingredients to synthesize spinel by means of powder metallurgy. We studied the preparation technology and the characteristics of the cermet material at first, then we tried to add small amount of superaddition for improve its performance such as conductivity and corrosion resistance. The results showed that the foreign additive containing different chemical valence ion from Ni2+ and Fe3+ could significantly refine characteristics of the cermet inert anode, and the inert anode based on NiFe2O4 spinel could be improved by the means of adding TiO2 and MnO2 to the ceramic phase.

12:00 PM

Aluminum Electrolysis Tests with Inert Anodes in KF-AlF3-Based Electrolytes: *Jian-Hong Yang*[1]; John N. Hryn[1]; Gregory K. Krumdick[1]; [1]Argonne National Laboratory

A low-temperature KF-AlF3-based electrolyte was used to perform aluminum electrolysis tests in a cell fitted with aluminum bronze metal anodes and wetted cathodes. Several 100A-100h tests were performed to investigate the effect of NaF concentration in the bath, current density, and temperature on cell operation. Results indicate that larger 1000A tests are warranted.

12:25 PM End

Amiya Mukherjee Symposium on Processing and Mechanical Response of Engineering Materials: NanoBehavior of Materials

Sponsored by: The Minerals, Metals and Materials Society, TMS Materials Processing and Manufacturing Division, TMS Structural Materials Division, TMS/ASM: Mechanical Behavior of Materials Committee, TMS: Shaping and Forming Committee
Program Organizers: Judy Schneider, Mississippi State University; Rajiv S. Mishra, University of Missouri; Yuntian T. Zhu, Los Alamos National Laboratory; Khaled B. Morsi, San Diego State University; Viola L. Acoff, University of Alabama; Eric M. Taleff, University of Texas; Thomas R. Bieler, Michigan State University

Monday AM — Room: 217C
March 13, 2006 — Location: Henry B. Gonzalez Convention Ctr.

Session Chairs: Rajiv S. Mishra, University of Missouri; Ruslan Z. Valiev, UFA State Aviation Technical University

8:30 AM Invited

Superplasticity in Nanostructured Materials: New Challenges: *Ruslan Z. Valiev*[1]; Rinat Islamgaliev[1]; [1]UFA State Aviation Technical University

Prof. A. K. Mukherjee laboratory's discoveries in 1999-2002 have revealed that nanostructured metals and alloys can demonstrate extraordinary superplasticity at low temperatures and/or high strain rates. This work presents the new results on superplasticity in several nanostructured Al and Ti alloys focusing on microstructure evolution and strain hardening, as well as the challenges of their application. Grain refinement in these alloys was accomplished using severe plastic deformation techniques, and subsequent superplastic deformation allowed not only to produce their efficient forming, but also increase significantly mechanical properties of the produced articles retaining the ultrafine-grained structure. For instance, using superplastic forming of nanostructured titanium we could process long-sized rods with extraordinary mechanical properties, e.g. yield stress over 1000 MPa and fatigue strength over 500 MPa. The obtained results demonstrate the possibilities of principally new applications of superplastic forming using nanostructured materials.

8:50 AM

Plasticity at Really Diminished Length Scales: *Alla V. Sergueeva*[1]; Nathan A. Mara[1]; Amiya K. Mukherjee[1]; [1]University of California

In recent years, the plastic behavior of technologically attractive nanocrystalline materials has become more prominent in the mainstream scientific community. In this work a review on the current understanding of the effects of microstructural characteristics on mechanical behavior of nanocrystalline materials produced by different methods including severe plastic deformation is presented. The microstuctural information with the mechanical data obtained from these nanoscale materials was analyzed in the context of plasticity at really diminished length scales. An experimental data arising from testing at different conditions clearly demonstrate that some microstructural features other than just grain size (grain boundary structure, grain size distribution, etc.) can also be responsible for the exhibited material behavior. Special emphasis is given to the difficulty of intragranular dislocation generation inside the matrix in truly nanoscale structure and its effect on accommodation processes in grain boundary mediated plastic behavior. This investigation is supported by NSF grant (NSF-DMR-0240144).

9:10 AM Invited

Mechanical Behavior of Nanocrystalline Metals: *K. Linga Murty*[1]; Ramesh K. Guduru[1]; Khaled M. Youssef[1]; Ronald O. Scattergood[1]; Carl C. Koch[1]; [1]North Carolina State University

Recent efforts have been very fruitful in producing artifact-free materials with nanosize grains less than 50nm. These nanograined metals exhibit very high strengths with reasonably good ductility. While there have been large amount of studies on hardness and strength characteristics, studies on strain-rate sensitivity are very limited. We describe here some of our recent work in characterizing SRS as well as activation volumes of nanograined metals using micro-tensile specimens. These tests have been carried out under iso-strain-rate conditions at ambient and we are in the process of evaluating these parameters using strain-rate jump tests during tensile loading. This work is supported in parts by the National Science Foundation grant #DMR-0201474 and by the Department of Energy grant #DE-FG02-02ER46003.

9:30 AM Invited

Influence of Specimen Size, Grain Size and Stacking-Fault Energy on the Mechanical Properties of Ultra-Fine Grained and Nanocrystalline Cu/Cu-Zn Alloys: *Yonghao Zhao*[1]; Xiaozhou Liao[2]; Yuntian Zhu[1]; Cheng Xu[3]; Zenji Horita[3]; Terence G. Langdon[3]; [1]Los Alamos National Laboratory; [2]University of Chicago; [3]University of Southern California

Much attention is currently devoted to the ductility achieved in nanocrystalline and ultrafined-grained materials. This report shows that several factors affect the ductility of tensile specimens including specimen size, grain size and the stacking-fault energy. Ultrafine-grained and nanocrystalline Cu/Cu-Zn alloys were prepared using different severe plastic deformation (SPD) techniques including equal-channel angular pressing (ECAP), high-pressure torsion (HPT), cold rolling and their combinations. It is shown in tensile testing that the ductility is reduced with decreasing specimen thickness and increased with decreasing specimen gauge length. With decreasing stacking-fault energy, the strain hardening of the samples increases thereby enhancing the tensile toughness. Evident strain hardening was observed in a nanocrystalline Cu-Zn alloy with a grain size smaller than 10 nm but there was no evident strain hardening in an ultrafine-grained Cu-Zn alloy. This paper discusses the origins of these effects.

9:50 AM Invited

Analysis of the Deformation Mechanisms in Bulk Ultrafine Grained Metallic Materials: *Igor V. Aleksandrov*[1]; Roza Chembarisova[1]; Vil Sitdikov[1]; [1]Ufa State Aviation Technical University

Numerous experimental investigations of the recent years demonstrate activation of specific mechanisms in the process of deformation of bulk ultrafine grained metallic materials processed by severe plastic deformation (SPD). In this report the results of analysis of microstructure evolution and deformation behavior on the example of pure copper subjected to high pressure torsion and equal-channel angular pressing are presented. The analysis was carried out with the help of computer simulation within the modified Estrin-Toth dislocation model. Upgrading of the model consisted in attempts to take into account specific features of SPD. The ob-

tained results of modeling are compared with the results of experimental investigations.

10:10 AM
Increase of Strength in Ni Due to Change of Methods of Severe Plastic Deformation: *Nikolay Krasilnikov*[1]; Georg Raab[2]; Witold Lojkowski[3]; Zbigniev Pakiela[4]; [1]Ulyanovsk State University; [2]Ufa State Avation Technical University; [3]Polish Academy of Sciences; [4]Warsaw University of Technology

In present work the influence of combinations of severe plastic deformation (SPD) methods on achievement of high strength of nickel is investigated. It is shown, that the change of scheme of SPD results in formation of a new type of structure in Ni, effective refinement of grains and an increase of structure uniformity, that enables to increase considerably the strength of metal. So the consecutive using of equal channel angular pressing, rolling and high-pressure torsion has allowed to generate homogeneous structure of Ni with grain size 120 nm. The samples obtained were characterized by record strength 1270 MPa. The analysis of deformation behavior of ultrafine grained Ni samples has shown, that the change of deformation mechanism of UFG metal is connected with activation of grain boundaries sliding already at room temperature.

10:30 AM Break

10:40 AM Invited
Verification of Constitutive Equation for Ultrafine Grain Ti-6Al-4V Alloy Based on Dislocation Mechanics: *Amit K. Ghosh*[1]; Peter Comley[1]; [1]University of Michigan

Precise simulation of superplastic forming process requires a precise description of constitutive equation at elevated forming temperature and over a wide range of strain rates. Tensile test to determine superplastic properties suffer from the problem that with increasing strain rate the distribution of strain within the specimen does not remain uniform, thereby making the values of measured stress and strain unreliable with increasing strain. Recent efforts to standardize the superplastic tensile test have revealed that strain hardening and softening rates increase with increasing strain rate, however, the measured stress-strain curves are not free from the uncertainties due to neck growth. Considering the hardening and softening effects, a dislocation mechanics based form of constitutive equation has been developed that permits one to distinguish between true material response and that due to necking effects. Verification of constitutive equation against experiments will be shown.

11:00 AM
Nanocrystalline Fe(Al,Si) Alloys: Hardening by Annealing: *T. D. Shen*[1]; John G. Swadener[1]; Jian Y. Huang[2]; Ricardo B. Schwarz[1]; [1]Los Alamos National Laboratory; [2]Boston College

We have used mechanical alloying (MA) to prepare single-phase nanocrystalline $Fe_{92}Al_2Si_6$ alloys with an average crystallite size of approximately 10 nm. The nanostructure is thermally stable to at least 450°C. The structural and mechanical properties were studied as a function of isochronal annealing treatments. After annealing at 450°C for 1 hour, the grain size remained almost constant, the dislocation density decreased by a fact of ten, and the hardness increased by ~ 20%. The increase in hardness is contrary to what one should expect from the changes in grain size and dislocation density. The data suggests that this abnormal behavior is caused by a strong increase in the solute-dislocation interaction (aging). Different models for the superposition of the dislocation and solute contributions to the strength of nanocrystalline alloys will be discussed.

11:20 AM Invited
Analysis of Strain Distribution in Equal Channel Angular Extrusion by Finite Element Method Simulation and Experimental Validation: Brett A. Pond[1]; *Shankar M. Sastry*[1]; [1]Washington University

Equal channel angular extrusion (ECAE) has been shown to produce ultra-fine grains in materials. Previous studies on ECAE consider only two-dimensional analysis on primarily low-temperature ECAE processing. The current study focuses on three-dimensional strain distribution in cylindrical samples resulting from ECAE processing at T > 0.4Tm. The effects of die geometry, sample size, friction coefficient, stress-strain behavior, and backpressure on strain distribution by ECAE are studied. The strain distributions is analyzed by a three-dimensional finite element computer program DEFORM 3D, as well as experimental measurements and validation.

11:40 AM Invited
Structure Formation, Phase Transformations and Properties in Cr-Ni Austenitic Steel after ECA Pressing and Heating: *Sergey Dobatkin*[1]; Olga Rybal'chenko[1]; Georgy Raab[2]; [1]A.A.Baikov Institute of Metallurgy and Materials Science; [2]Ufa State Aviation Technical University

It is shown that cold ECA pressing of 0.07%C – 17,3%Cr – 9,2%Ni – 0.7%Ti austenitic steel leads to formation of submicrocrystalline structure: generally oriented subgrains with separated grains (100-250 nm in size). The steel samples of 20 mm in diameter and 80 mm in length were subjected to ECAP at room temperature for 4 passes. The angle between the channels was 120°. ECAP promotes the martensitic transformation which becomes more active only at N = 4, leading to the formation of 45% martensite. During heating the fraction of high angle boundaries as well as volume of austenite is increased and structure become more equiaxed. Submicrocrystalline structure with grain size 150-250 nm and 80% of austenite was obtained at heating to 550° C.Such structure exhibits a substantial strain hardening to YS = 1090 MPa relative to the initial state (YS = 320 MPa) and EL = 12%.

12:00 PM
Influence of Sputter-Deposition Rate on Microstructures and Mechanical Properties of 330 Stainless Steel Thin Films with Nanoscale Growth Twins: *Xinghang Zhang*[1]; Amit Misra[2]; Richard G. Hoagland[2]; [1]Texas A&M University; [2]Los Alamos National Laboratory

We have recently synthesized single-phase 330 stainless steel (330 SS) thin films with a high density of growth twins, oriented parallel to the film surface and separated, on average, by a few nanometers. Sputter-deposited 330 SS films have the same face-centered-cubic structure as their bulk counterpart. However, the strength of as-deposited 330 SS films, derived from nanoindentation hardness measurement, is about an order of magnitude higher than that of bulk 330 SS. In twinned structures with average twin spacing of a few nanometers, plasticity may be controlled by the motion of single rather than pile-ups of dislocations. By varying sputter-deposition rate, we have changed the average twin spacing in 330 SS films. A decrease in hardness is observed in 330 SS films with enlarged twin spacing. The formation mechanism of twin nuclei is explained using an analytical model, which shows the nucleation of growth twins is influenced by sputter-deposition rate.

12:20 PM
Mechanical Behavior of Nano-Laminate Cu Foils Synthesized by Multilayer Technology: *Andrea M. Hodge*[1]; Yinmin Morris Wang[1]; Troy W. Barbee Jr.[1]; [1]Lawrence Livermore National Laboratory

Atomic level deposition of layers by magnetron sputtering enables the fabrication of free-standing nano-laminate foils. In this talk, we report results on high purity (99.999%), fully dense, free-standing Cu/Cu nanolaminates composed of sixty-eight thousand (68,000) 2.5 nanometer-thick Cu layers for a total sample thickness of ~170 microns. Extensive plan view and cross-section transmission electron microscopy (TEM) demonstrate the nanostructured nature of the Cu/Cu multilayers, a very low apparent dislocation density and medium density growth twins. Tensile tests were performed in air and in liquid nitrogen using 6.0 mm gauge length dogbone-shaped samples. All samples studied exhibited a yield point, subsequent localized deformation within the initial shear band, and no evidence of work hardening. Overall the Cu/Cu nano-laminates had high yield strength (> 550 MPa) fracturing by near knife edge ductile necking within the first shear band formed.

Biological Materials Science: Implant Biomaterials

Sponsored by: The Minerals, Metals and Materials Society, ASM International, TMS Structural Materials Division, TMS: Biomaterials Committee, TMS/ASM: Mechanical Behavior of Materials Committee
Program Organizers: Andrea M. Hodge, Lawrence Livermore National Laboratory; Chwee Teck Lim, National University of Singapore; Richard Alan LeSar, Los Alamos National Laboratory; Marc Andre Meyers, University of California, San Diego

Monday AM Room: 212A
March 13, 2006 Location: Henry B. Gonzalez Convention Ctr.

Session Chairs: C. T. Lim, National University of Singapore; Jikou Zhou, Lawrence Livermore National Laboratory

8:30 AM
Mini-Implant for Orthodontic Anchorage: *Carlos Nelson Elias*[1]; Liliane Siqueira Morais[1]; Glaucio Serra Gumaraes[1]; [1]Instituto Militar de Engenharia

In an orthodontic treatment, one way of having teeth movement done with minimal undesired movement is by having a large anchorage group of teeth. Another way of obtaining anchorage is by using an extraoral arch, which needs great co-operation by the patient. The third orthodontic ancorage process is by using an osseointegrated titanium implants. In this case the implant can be surgically removed after the orthodontic treatment. Nowdays, an orthodontics mini-implants has been used to anchor different movements such as the intrusion of anterior and posterior teeth, mesio-distal teeth, space closure, upright of posterior teeth, extrusion of impacted teeth, orthopedic traction and expansion of maxillary suture. The purpose of this work was to analyze the bone reactions of immediately loaded mini-implants of titanium alloy (grade 5) by histological, histomorphometrical and mechanical parameters. The present study used eighteen New Zealand White rabbits. The mechanical properties of mini-implant has been determined.

8:50 AM
Substrate Creep Effects on the Fatigue Behavior of a Dental Restoration Structure: *Jikou Zhou*[1]; Min Huang[2]; Wole O. Soboyejo[2]; [1]Lawrence Livermore National Laboratory; [2]Princeton University

This paper investigates the effects of substrate creep on the fatigue behavior of a multilayer dental restoration model structure. Two sets of specimens with different subsurface crack sizes were prepared. Each set of specimens was tested with increasing load levels until the top glass failed monotonically. The results showed that at high load levels (higher than 60 N), slow crack growth is the major fatigue mechanisms; while fatigue life is significantly degraded by the substrate creep under low cyclic load levels (less than 60 N), in which longer testing duration involved. A previously established substrate creep model was then modified, and was successfully fitted to the experimental data.

9:10 AM
Mechanical Properties and Biocompatibility of Laser-Deposited Orthopaedic Alloys: Soumya Nag[1]; *Rajarshi Banerjee*[2]; Hamish L. Fraser[1]; [1]Ohio State University; [2]University of North Texas

Due to the rapidly increasing number of surgical procedures involving prosthesis implantation, there is an urgent need for improved biomaterials and processing technologies for orthopaedic implants such as hip implants. By employing novel near-net shape processing technologies, such as laser engineered net shaping (LENS™), it is possible to rapidly manufacture custom-designed implants. From the materials perspective, orthopaedic alloys for implant applications typically require a combination of appropriate mechanical and osseo-integration properties. Since the beta phase in Ti alloys exhibits a favorable balance of properties, there is a thrust towards the development lower modulus beta-Ti alloys. The present paper will discuss the microstructure and mechanical properties of beta Ti alloys deposited using LENS™ for orthopaedic applications. In addition, the biocompatibility of these materials will also be assessed via in vitro studies and the results discussed in this presentation.

9:30 AM
A Novel Combinatorial Approach to the Development of Metallic Biomaterials for Orthopaedic Implants: *Soumya Nag*[1]; Rajarshi Banerjee[2]; Hamish L. Fraser[1]; [1]Ohio State University; [2]University of North Texas

Metallic biomaterials for orthopaedic implant applications typically require a combination of appropriate mechanical properties with excellent biocompatibility including osseo-integration properties. In recent years there has been a thrust towards the development lower modulus beta-Ti alloys for implant applications. While a number of biocompatible beta-Ti alloys have been reported in recent literature, there is still a large scope for improvement in terms of alloy design via optimization of alloy composition and thermo-mechanical treatments. A novel combinatorial approach has been developed for understanding composition-microstructure-property relationships in these alloys. This approach is based on the use of directed laser deposition to rapidly process compositionally graded alloys, administer appropriate heat-treatments, characterize and quantify their microstructures, assess their mechanical properties, and finally develop composition-microstructure-property relationships. This combinatorial approach will be employed for studying the binary, Ti-Ta, and Ti-Nb, as well as the ternary Ti-Nb-Ta, and quaternary Ti-Nb-Zr-Ta systems, which are promising for implant applications.

9:50 AM
Biocorrosion Behaviour of Magnesium Alloys as Degradable Metallic Biomaterials: *Hao Wang*[1]; Mingxing Zhang[1]; Zhiming Shi[1]; Ke Yang[2]; [1]University of Queensland; [2]Chinese Academy of Sciences

Drawbacks associated with permanent metallic implants lead to the search for degradable metallic biomaterials. Magnesium alloys have been highly considered as Mg is essential to bodies and has a high biocorrosion potential. In this study, corrosion behaviour of pure magnesium and magnesium alloy AZ31 in both static and dynamic physiological conditions (Hank's solution) has been systematically investigated. It was found that both materials degraded fast at beginning, then stabilised at a rate of 0.5mm/year. The mechanical properties of the materials also decreased with immersion time. The electrochemical tests indicated that the AZ31 had a lower anodic polarisation current and high polarisation resistance in the first 100h, indicating a more stable protection film was formed. For static applications (hard issue replacements), the hydrogen release might be an issue, while for dynamic applications (stents), constant pH resulted in a high degradation rate. Surface coating has been developed to achieve a controllable biodegradation.

10:10 AM Break

10:30 AM
Compare Corrosion Resistance and Wear Resistance of Boronized Ti-6Al-4V with Stainless Steel Used as Medical Implants: *Roumiana Petrova*[1]; Boris Goldenberg[1]; Naruemon Suwattananont[1]; [1]New Jersey Institute of Technology

The use of titanium and its alloy has increased over the past years as medical implants, but wear resistance and corrosion resistance have limited its use in hip and other joints replacements. The present study describes investigation of boron coating on stainless steel compared with alloy Ti-6Al-4V. The coatings were produced by a thermo-chemical treatment with an original technology powder mixture at a temperature range of 850-1050°C. Metallographic examination, x-ray diffraction, and microhardness testing were used to determine the characteristics of the diffusion layer. The potentiodynamic polarization measurements were used to investigate the corrosion resistance. It was shown that the boronizing process created a boride layers with a thickness of 10-15 μm depending on substrates, temperatures, and time, with microhardness of about 4-6 times greater than that of the substrate. The corrosion and wear resistance of the boronized coating was determined to be better than that of the substrate.

10:50 AM
Evaluation of Attachment, Differentiation, and Growth of MC3T3-E1 Osteoblasts on Ti-Al-Nb Alloys: *Jeffrey P. Quast*[1]; Melissa J. Baumann[1]; Carl J. Boehlert[1]; [1]Michigan State University

To date, the most common material choice for load bearing implants is titanium-aluminum-vanadium (Ti-Al-V) alloys. However, the substitution

of V for niobium(Nb) has produced an alloy with mechanical properties that more closely match bone. In this study, growth and differentiation of MC3T3-E1 osteoblasts on two alloys, Ti-15Al-33Nb(at%) and Ti-21Al-29Nb(at%), were compared to that on Ti-6Al-4V(wt%). Osteoblasts(Obs) were plated onto 2cm x 2cm square samples at a concentration of 11,320 cells/cm^2, and grown at 37°C in a humidified atmosphere of 95% air and 5% CO_2. OBs were fed with alpha-MEM supplemented with 10% fetal bovine serum. Cell attachment was measured after 2 and 4 days using a hemocytometer. Scanning electron microscopy and optical microscopy were also employed to compare cell attachment behavior. Preliminary data has shown little variance in attachment and differentiation among the three different alloys. The implications of these results on the future of implant design will be discussed.

11:10 AM

Grindability of Ti-Alloys for Dental Applications: *Kwai S. Chan*[1]; Marie Koike[2]; Masafumi Kikuchi[3]; Osamu Okuno[3]; Toru Okabe[2]; [1]Southwest Research Institute; [2]Baylor College of Dentistry; [3]Tohoku University

The grindability of Ti-based alloys for dental applications was analyzed by considering the fracture behavior of individual alloys in response to the stress field of a grinding wheel. The stress field was computed by treating the grinding wheel as a cylindrical disk with a flat region acting on a flat substrate. The initiation and propagation of microcracks in the substrate was examined on the basis of the contact stress field and a set of fracture criteria. Grindability was computed as a function of grinding speed for Ti-based alloys containing an alpha, alpha + beta, or beta microstructure with or without intermetallic precipitates. The theoretical results are compared against experimental data to elucidate the role of microstructure in grindability. The comparison revealed that alloying addition that leads to the formation of brittle intermetallics enhances grindability by reducing fracture toughness, tensile ductility, and the resistance to crack initiation and propagation.

11:30 AM

A Degradation Study of Poly (DL-Lactide) Bone Plate and Screw for Fracture Fixation: *Carlos Nelson Elias*[1]; Ana Maria Bolognese[2]; Aleandre Ribeiro[2]; [1]Instituto Militar de Engenharia; [2]Universidade Federal do Rio de Janeiro

Some polymer are used for the controlled delivery of protein and peptide drugs, for the manufacture of medical devices and wound dressings as well as for fabricating scaffolds in tissue engineering. In the present study bone plates and screws for fixation of mandibular and zygomatic fractures of PDLLA (poly-DL-lactic acid) from Purac (Biochem Gorinchem, The Netherlands) were made. These materials are useful for a bone fixation, cartilage repair, and drug delivery. The kinetics of the polymerizations were followed by DSC, and the mechanical behavior was monitored as a function of temperature to obtain the Tg. Plates were subjected to hydrolytic degradation in an aqueous phosphate buffer solution at a pH 7 and 37°C. Degradation as function of time was studied via tensile testing and scanning electron microscopy observation after 10, 20, 30 and 40 days aqueous solution immersion. Complete degradation had not occurred by the end of the study.

11:50 AM

Cell Formation Enhancement on Ultrafine Grained Orthopedic Ti and Ti Alloy Surfaces: Chang Yao[1]; *Thomas Webster*[1]; Henry J. Rack[2]; [1]Purdue University; [2]Clemson University

Previous investigations have shown that ultra-fine grain sizes formulated by severe plastic deformation have the potential for materially enhancing the mechanical performance of titanium alloys. These achievements are of particular interest to the orthopedic community since these alloys, i.e., c.p. Ti (grade 2 and grade 4) and Ti-6Al-4V, constitute the vast majority of titanium alloys currently used for biomedical devices. However, little is known about their ability to support new bone growth. This presentation will examine the cellular response of these systems as determined through in-vivo and in-vitro investigations. These biological studies provided evidence of greater osteoblast (bone-forming cell) functions on UFG compared to currently-used Ti and Ti6Al4V. For example, osteoblast cell adhesions were up to 40-60 % greater when surface features were decreased from conventional (micron) to biologically-inspired regimes for c.p. Ti. In summary, UFG c.p. Ti and Ti6Al4V provide substantial promise for enhancing the performance of orthopedic devices.

12:10 PM

Prototyping the Dental Materials Data Warehouse for Materials Selection: *Yong Li*[1]; [1]IMS

In this project, the effectiveness of the new data management technique of data warehousing was critically evaluated for integrating dental materials data, in order to facilitate the informational services including data retrieval and materials selection for dental materials. A scaled-down version of the dental materials data warehouse was successfully constructed and an English Query application, which allows the end users to formulate their queries in natural English language, was developed on top of the data warehouse. The current application supports five types of queries from basic practice of data access and retrieval to more advanced information analytical service of materials selection. The results demonstrate that the data warehousing technique is of a great potential in storing, processing and managing dental materials data, and will have a significant impact on research, education and operation in the dental materials community.

Bulk Metallic Glasses: Elastic, Plastic Behavior, and Computation

Sponsored by: The Minerals, Metals and Materials Society, TMS Structural Materials Division, TMS/ASM: Mechanical Behavior of Materials Committee
Program Organizers: Peter K. Liaw, University of Tennessee; Raymond A. Buchanan, University of Tennessee

Monday AM — Room: 217B
March 13, 2006 — Location: Henry B. Gonzalez Convention Ctr.

Session Chairs: Peter K. Liaw, University of Tennessee; William L. Johnson, California Institute of Technology

8:30 AM Keynote

Plastic Yielding, Flow, and Configurational Entropy in Metallic Glasses: *William L. Johnson*[1]; [1]California Institute of Technology

Metallic glasses are "atomic" solids in which the potential energy depends mainly on atomic density and centro-symmetric pair potentials. The bonding is weakly directional. Deformation is dominated by the stress driven cooperative shear motion of large atomic clusters (called shear transformation zones or STZ's) between intrinsic glass configurations. A model for the yielding and plastic flow is presented based on a decription of "average" properties STZ's. The fundamental properties of STZ's are related to the configurational entropy and elastic properties (G,B, and Poisson's ratio) of the glass and liquid. The model predicts that all metallic glasses share certain universal characateristics while the material specific properties are primarily attributable to variations in the Poisson Ratio among metallic glasses. Topics will include plastic yeilding and flow in the glass, liquid viscosity and liquid fragility. The discussion will include extensive comparison of the model with experimental observations.

9:00 AM Invited

Statistics of Shear Band Activation in Metallic Glasses: *Christopher A. Schuh*[1]; Corinne E. Packard[1]; [1]Massachusetts Institute of Technology

The in-situ study of shear localization in metallic glasses is difficult using conventional mechanical tests, because shear bands form very quickly and their preferred formation sites are not known a priori. Using instrumented nanoindentation, shear bands can be induced in specified locations, under a well-defined stress state. In this presentation our latest work using this technique will be outlined, focusing upon the statistics of shear band activation in bulk glass forming alloys. Significant scatter is found in the stress state at yield, and analysis techniques are presented to assess whether the scatter arises due to variations in the glass structure or due to thermal activation effects.

9:25 AM Invited

Strain-Rate Dependence of Shear-Band Behavior and Serrated Flow in a Metallic Glass: *Michael Atzmon*[1]; Wenhui Jiang[2]; [1]University of Michigan; [2]University of Tennessee

Nanoindentation of a metallic glass leads to the formation of shear bands, the density of which increases with displacement rate. At low displacement rates, pronounced serrations, i.e., displacement bursts, are observed in the load-displacement curves. In an effort to improve the understanding of shear band behavior, we have conducted nanoindentation studies of amorphous Al86.8Ni3.7Y9.5 at varying rates. The initial amount and distribution of free volume were varied by cold rolling and/or annealing. Not only the density of shear bands, but their shape is dependent on the strain rate. The results are examined using both an accepted microscopic model and continuum analysis. The microscopic model alone cannot account for the observed trends, but combination of the microscopic model and 3-D continuum mechanics explains several observed trends. The results suggests that a high shear-band propagation velocity is required for serrations to be observed.

9:50 AM

Rate-Dependent Shear Banding in a Zr-Based Bulk Metallic Glass: *W. H. Jiang*[1]; G. J. Fan[1]; H. Choo[1]; P. K. Liaw[1]; [1]University of Tennessee

Metallic glasses exhibit the inhomogeneous plastic deformation at low temperatures and high strain rates. The inhomogeneous deformation concentrates on highly-localized, narrow, shear bands. Shear banding affects substantially the plastic-flow behavior. It has been demonstrated that the shear-band formation is dependent on strain rates during indentation[1]. However, we are not aware of any research addressing this rate-dependence in uniaxially loading. Using geometrically-constrained samples, we investigated the shear-band formation at various strain rates in uniaxial compression. The results will be compared with the numerical calculations using the free volume model[2]. The present work is supported by the National Science Foundation International Materials Institute (IMI) program, under DMR-0231320, with Dr. C. Huber as the program director. [1]W. H. Jiang and M. Atzmon, J. Mater. Res., 2003, 18, 755. [2]P. S. Steif, F. Spaepen, and J.W. Hutchinson, Acta Metall. 1982, 30, 477.

10:10 AM

Strain Rate Effects on the Mechanisms of Deformation and Nanocrystallization in Bulk Metallic Glasses: *Anantharamakrishnan Puthucode*[1]; Rajarshi Banerjee[1]; Suman Vadlakonda[1]; Michael Kaufman[1]; [1]University of North Texas

Nanoindentation loading curves frequently display pop-ins at low loading rates but not at higher loading rates. These "pop-ins" reportedly correspond to the activation of shear bands, which are readily resolved at the lower rates. Several reasons for their loss at higher loading rates have been speculated including instrumental resolution, homogenization of shear bands and, more recently, strain-induced free volume effects. In this study, a series of indents were made on a Zr-based BMG composition at different strain rates (displacement-controlled) and, indeed, the pop-ins blur with increasing strain-rate. In order to understand this strain-rate dependence and the possibility of nanocrystallization accompanying the localized deformation, TEM samples were cut from the indented regions using a focused ion beam and examined by analytical high resolution TEM methods. Similar studies were performed on an Al-based BMG in order to determine whether the results are alloy specific or more general to this class of materials.

10:30 AM Break

10:40 AM Invited

Temperature Dependence of the Elastic Constants of Metallic Glasses and Single Crystals: *Ricardo B. Schwarz*[1]; D. J. Safarik[1]; [1]Los Alamos National Laboratory

The low-temperature elastic properties of metallic glasses show various anomalies not found in crystalline alloys. We have measured the elastic constants of the glass and single crystal $Pd_{40}Cu_{40}P_{20}$ over the range $4 < T < 300$ K. The glass shear modulus is 15-60% lower than that the lowest shear modulus in the crystal (the tetragonal symmetry $Pd_{40}Cu_{40}P_{20}$ crystal has 4 independent shear moduli). For $4 < T < 15$ K, the shear modulus of the $Pd_{40}Cu_{40}P_{20}$ crystal decreased as T^4, which is the normal trend for crystals, attributed to the anharmonicity of the lattice vibrations. Over the same temperature range, the shear modulus of the $Pd_{40}Cu_{40}P_{20}$ glass decreases linearly with temperature. We describe the linear temperature dependence of the glass shear modulus in terms of anelastic relaxations involving groups of atoms. We discuss the origin of these relaxations in terms of atomistic models for the glassy structure in metals.

11:05 AM

Elastic Properties of Ca-Based and Zr-Based Bulk Metallic Glasses Studied by Resonant Ultrasound Spectroscopy: *Zhiying Zhang*[1]; Raphaël P. Hermann[1]; Veerle Keppens[1]; Mark L. Morrison[1]; Guojiang Fan[1]; Peter K. Liaw[1]; Oleg N. Senkov[2]; Daniel B. Miracle[3]; Yoshihiko Yokoyama[4]; [1]University of Tennessee; [2]UES Inc.; [3]Air Force Research Laboratory; [4]Tohoku University

Resonant ultrasound spectroscopy (RUS) yields the elastic constants for millimeter-sized samples simultaneously and nondestructively. In this work, the elastic properties of the Ca-based bulk metallic glasses (BMGs), Ca65Mg15Zn20, Ca50Mg20Zn30 and Ca55Mg18Zn11Cu16, were investigated by RUS as a function of temperature between 2 and 400 K, which is close to and above the glass-transition temperature of these alloys. In addition, the elastic properties of the Zr-based BMGs, Zr50Cu40Al10, Zr50Cu30Ni10Al10 and Zr52.5Cu17.9Ni14.6Al10Ti5, were studied as a function of temperature between 2 and 400 K. Results show that both the Young's modulus and the shear modulus decrease with increasing temperature. On the other hand, Poisson's ratio increases with increasing temperature. The influence of the composition on the fragility, the glass-forming ability and mechanical properties of BMGs will be discussed. The present work is supported by NSF DMR-0206625 and NSF IMI DMR-0231320, with Dr. C. H. Huber as the program director.

11:25 AM Invited

Calculated and Measured Elastic Constants of Zr50Cu(40-x)Al10Pdx Metallic Glasses: *Don M. Nicholson*[1]; V. Keppens[2]; Z. Zhang[2]; R. Hermann[2]; Y. Yokoyama[3]; Gongyao Wang[2]; P. K. Liaw[2]; Akihisa Inoue[3]; [1]Oak Ridge National Laboratory; [2]University of Tennessee; [3]Tohoku University

Recent studies correlate the elastic constants with the mechanical behavior of bulk metallic glasses (BMGs). In particular, BMGs with higher toughnesses exhibit greater Poisson's ratios. It has been found that the addition of the 3 atomic percent of Pd in the Zr-Cu-Al BMGs significantly improves the fatigue strength, relative to other Zr-based BMGs. Moreover, the improved fatigue resistance was found to be related to the high ratio of the shear modulus to bulk modulus, and, thus, the high Poisson's ratio in the Zr-Cu-Al-Pd BMG. To understand the role of Pd, we measured and calculated elastic constants of Zr50Cu(40-x)Al10Pdx. The calculations employ the ab initio molecular dynamics of liquids instantaneously quenched to a glass. The distribution of the free volume and elastic constants are predicted for the glass structures. The elastic constants are also measured, using the Resonant Ultrasound Spectroscopy.

11:50 AM Invited

Applications of Metallic Glasses: Thin Films and Nanostructured Parts: *Jinn P. Chu*[1]; Chun Ling Chiang[1]; Hadi Wijaya[1]; Chih Wei Wu[1]; [1]National Taiwan Ocean University

Considerable progresses in the processing of bulk metallic glasses (BMG) have been attained recently. In this presentation, the potential applications of metallic glasses in the fields of thin films and nanostructured parts are given. First, the annealing-induced extensive amorphization in glass-forming thin films in the supercooled liquid (SCL) region is reviewed. Controllable extensive amorphization is useful to regulate specific film properties such as electrical and magnetic properties. Materials structured on the nanometer scale give rise to many interesting new properties and phenomena, which lead to a wide variety of linear and nonlinear device applications. In the second part of the presentation, properties of nanostructured BMG prepared by superplastic-forming in SCL region in air are presented. Characterization results based on transmission and scanning electron microscopes, atomic force microscopy and optical properties performed on nanostructured BMG are discussed.This work was supported by the National Science Council of Taiwan (NSC 93-2216-E-019-007, 94-2218-E-110-009).

12:15 PM

Molecular Dynamics Simulations for the Effect of Hydrogen on the Mechanical Behavior of an Amorphous Metal: *Pil-Ryung Cha*[1]; Yu-Chan Kim[2]; Ki-Bae Kim[2]; Hyun-Kwang Seok[2]; [1]Kookmin University; [2]Korean Institute of Science and Technology

Using molecular dynamics simulations, with a realistic many-body embedded-atom potential, and a novel method to characterize local order, we study the structural stabilities of amorphous nickel systems with different amount of hydrogen and the effect of hydrogen on the structural change of the system during loading. We find the nonlinear increase of atomic volume of amorphous Ni with increasing hydrogen concentration while crystalline Ni shows linear increase. We also find crystallization of amorphous Ni at room temperature above a critical hydrogen concentration (the crystallization temperature (Tx) of pure amorphous Ni is between 500 and 600 K) and the decrease of its Tx with increasing hydrogen concentration. We call the above enhanced crystallization of amorphous nickel hydrogen-induced crystallization (HIC) and discuss its microsopic mechanism.

Cast Shop Technology: The Aluminum Fabrication Industry: Global Challenges and Opportunities: Aluminum Plenary Session

Sponsored by: The Minerals, Metals and Materials Society, Aluminum Association, TMS Light Metals Division, TMS: Aluminum Committee
Program Organizers: Subodh K. Das, Secat Inc; Michael Hal Skillingberg, Aluminum Association; Ray D. Peterson, Aleris International; Rene Kieft, Corus Group; Travis J. Galloway, Century Aluminum Company

Monday AM — Room: Theater
March 13, 2006 — Location: Henry B. Gonzalez Convention Ctr.

Session Chair: Subodh K. Das, Secat Inc

See The Aluminum Fabrication Industry: Global Challenges and Opportunities Symposium on page 47 for presentations.

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

Sponsored by: The Minerals, Metals and Materials Society, TMS Extraction and Processing Division, TMS: Materials Characterization Committee
Program Organizers: Jiann-Yang James Hwang, Michigan Technological University; Arun M. Gokhale, Georgia Institute of Technology; Tzong T. Chen, Natural Resources Canada

Monday AM — Room: 206A
March 13, 2006 — Location: Henry B. Gonzalez Convention Ctr.

Session Chairs: Yoshiaki Umetsu, Tohoku University; John E. Dutrizac, CANMET-MMSL

8:30 AM

Characterization of the Cr(lll) Analogues of Jarosite-Type Compounds: *John E. Dutrizac*[1]; Tzong T. Chen[1]; [1]CANMET- Mining and Mineral Science Laboratories

A new class of compounds, the Cr(lll) analogues of jarosite-type compounds (MCr3(SO4)2(OH)6, where M is H3O, Na, K, Rb, Tl, Ag, NH4 or Pb2+), was synthesized at 230°C using either Cr(SO4)1.5 or CrCl3 media. X-ray diffraction analysis confirmed that the new compounds were well crystallized and had the structure characteristic of both natural and synthetic jarosites. The morphology of the precipitates was characterized by scanning electron microscopy (SEM) of both loose powers and polished cross sections of the various precipitates. Typically, the precipitates consist of tiny cauliflower-like agglomerates; discrete crystals are rare despite the high synthesis temperatures employed. Electron microprobe analyses confirmed the bulk chemical assays of the various precipitates and demonstrated the homogeneity of the compounds. Overall, the characterization results suggest that the Cr(lll) analogues of jarosite-type compounds formed by the in situ crystallization of an initially formed amorphous chromium oxyhydroxide gel.

8:55 AM Invited

Iron Removal from Titanium Ore by Electrochemical Method: *Obana Isao*[1]; Toru H. Okabe[1]; [1]University of Tokyo

With the objective of establishing a new titanium production process, a novel process for the selective removal of iron from titanium ore by an electrochemical method was investigated. The thermodynamic analyses of the chlorination reactions in a Ti-Fe-O-Cl system were carried out prior to the fundamental experimental work, and the possibility of the chlorination reactions was investigated. In the experiment, low-grade titanium ore in a carbon crucible was immersed in molten calcium chloride and polarized anodically at 1100 K under an argon atmosphere in order to remove iron from the ore. At this stage, 80 mass% of iron in the low-grade titanium ore was successfully removed. This result shows that iron in the titanium ore was chlorinated and removed by the electrochemical method.

9:20 AM Invited

Some Reactions of MgO in the MgO-Based Binder Materials for Slurried Soils in the Aqueous Media under a Flow of CO_2: Tomohito Kameda[1]; Jun Ishikawa[1]; Tetsuo Shirota[1]; *Yoshiaki Umetsu*[1]; [1]Tohoku University

The MgO-based binder materials applicable to slurried soils and, sometimes, to contaminated wet soils have been paid attention to because of the moderate nature of MgO in exposure to natural environment. For investigation of the behaviors of MgO during soil-binding process, reactions of MgO in suspension in water have been determined in the presence of CO_2 at different partial pressures and temperatures by X-ray diffraction and morphology observation of the solid phase and monitoring of the solution pH. Under CO_2 stream in the aqueous phase, MgO was found to be easily leached and then needle-shaped crystals of $MgCO_3 \cdot 3H_2O$ with hexagonal cross section were precipitated at a higher CO_2 partial pressure at temperatures lower than about 50°C. At lower CO_2 partial pressure or high temperatures, $MgCO_3 \cdot 3H_2O$ was precipitated first and then converted into very thin, flaky crystals of basic magnesium carbonate.

9:45 AM Invited

The Effect of the Mineralogy of the Platinum Group Metals on Their Recovery and Leachability: *Cesar Joe Ferron*[1]; Chris C. Hamilton[1]; O. Valeyev[1]; [1]SGS Lakefield Research Limited

The mineralogy of the platinum group minerals is fairly complex, and it is therefore not surprising that the different minerals have variable response to metallurgical processes, in particular, flotation and leaching. 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 cooperate PtS. Further work showed that a thermal pretreatment at 500-700°C transformed the structure of the cooperate 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 thermal pretreatment.

10:10 AM Break

10:20 AM

Materials Characterization of Electrocoagulation By-Products Using Al-Fe Combination Electrode System: *Jewel A. Gomes*[1]; Praveen Daida[1]; George Irwin[1]; Hylton McWhinney[2]; Tony Grady[2]; Hector Moreno[1]; Eric Peterson[3]; Jose R. Parga[4]; David L. Cocke[1]; [1]Lamar University; [2]Prairie View A&M University; [3]Highland Community College; [4]Institute Technology of Saltillo

Electrocoagulation (EC) has been performed with Al-Fe electrode system with changing polarity for the removal of arsenic from water. The removal process has been studied using ICP-AES and Anodic Stripping Voltammetry with a wide range of arsenic concentration (1-1000 ppm) at various pH (4-10) and residence times (1-60 min). Electrochemically gen-

erated by-products have been analyzed using XRD, FTIR, XPS, SEM/EDS and Mössbauer Spectroscopy. Results revealed expected crystalline iron oxides (magnetite (Fe3O4), lepidocrocite (FeO(OH)), iron oxide (FeO)) and aluminum oxides (bayerite (Al(OH)3), diaspore (AlO(OH)), mansfieldite (AlAsO4·2(H2O)), as well as some interactions among the phases. The amorphous or ultra-fine particular phase was also found in the floc. The substitution of Fe3+ ions by Al3+ ions in the solid surface has been observed, indicating an alternative removal mechanism of arsenic in these metal hydroxides and oxyhydroxides by providing larger surface area for arsenic adsorption via retarding the crystalline formation of iron oxides.

10:45 AM

Microtexture and X-Ray Nanotomography of a Silver-Bearing Siliceous Ore: *Tzong T. Chen*[1]; Alexander Sasov[2]; John E. Dutrizac[1]; Peter D. Kondos[3]; Glenn Poirier[1]; [1]CANMET- Mining and Mineral Sciences Laboratories; [2]SkyScan; [3]Barrick Gold Corporation

Drill core samples containing 16-127 ppm Ag were analyzed by SEM and X-ray nanotomography to determine the occurrences of the Ag and the microtexture of the siliceous matrix. The core samples consist essentially of porous masses of quartz and amorphous silica that contain abundant pores which have sizes ranging from less than 1 micrometer to several millimetres. The pores seem to have only limited connections to one another. The fine pore sizes, together with the limited pore connections, greatly reduce the permeability of the core samples. Silver occurs mainly as less than 1 micrometer-sized particles of silver sulphide and, in subordinate amounts, as silver-copper sulphide, silver chloride, silver iodide, native silver and silver selenide. These minerals commonly occur embedded in the quartz matrix adjacent to the micrometer-sized pores. Intergrowths of silver sulphide with pyrite, silver chloride, or mercury chloride are common.

11:10 AM

Applied Mineralogical Studies on Colombian (Bagre, Antioquia) Black Sands: *Clara María Lamus Molina*[1]; Marco Antonio Márquez Godoy[1]; José Carlos Gaspar[2]; [1]Universidad Nacional de Colombia; [2]Universidade de Brasília

The following minerals found in the residual black sands from gold mining in El Bagre, Antioquia(Colombia) were identified as having major economic interest: ilmenita (FeTiO3), with an average of 49% of TiO2, frequently altered presenting crowns, lamellaes of rutile and alteration textures; titanomagnetite with up to 25% of TiO2; magnetite (Fe3O4) in individual grains or associated with others minerals as hematite and ferromagnesian silicates; rutile (TiO2) with considerable quantities of Nb2O5 (0.1-3.7% weight); zircon (ZrSiO4) with 66% weight of ZrO2, and monazite with an average of 63.43% weight of REE, this frequently associated to xenotime and thorite forming textures as little drops. Analysis in EPMA and SEM/EDS showed percentages of minor elements and traces, thereby clearly establishing the applications of these minerals in diverse industries. Furthermore, a detailed granumetric study of the different minerals and textural relationships among them also allowed for establishing the basis for possible processing and exploitation.

Computational Thermodynamics and Phase Transformations: Atomic Modeling Based Alloy Thermodynamics I

Sponsored by: The Minerals, Metals and Materials Society, TMS Electronic, Magnetic, and Photonic Materials Division, TMS Materials Processing and Manufacturing Division, TMS Structural Materials Division, TMS: Chemistry and Physics of Materials Committee, TMS/ASM: Computational Materials Science and Engineering Committee
Program Organizers: Dane Morgan, University of Wisconsin; Corbett Battaile, Sandia National Laboratories

Monday AM — Room: 210A
March 13, 2006 — Location: Henry B. Gonzalez Convention Ctr.

Session Chairs: John Rodgers, Innovative Materials Technologies, Inc; Gerbrand Ceder, Massachusetts Institute of Technology

8:30 AM Invited

Ab Initio Thermodynamic Modeling of Multicomponent Alloys: *Axel Van De Walle*[1]; Mark D. Asta[1]; Gautam Ghosh[1]; [1]Northwestern University

The construction of multicomponent thermodynamic databases is often limited by the amount experimental data available and the costs associated with collecting such data. Ab initio calculations of solid state alloy thermodynamics provide a quick and cost effective way to gather large amounts of thermodynamic data suitable for the construction of multicomponent thermodynamic databases. The algorithms and computational tools included in the Alloy Theoretic Automated Toolkit that enable this approach will be discussed. Special attention with be devoted to the determination of free energies via thermodynamic integration coupled with Monte Carlo simulations using new algorithms specifically designed to deal with the high-dimensionality of composition space in multicomponent alloys. Algorithms based on stochastic sampling are ideally suited for this task and offer the additional advantage of being naturally parallelizable.Examples of application to the Fe-Ni-Co-Cr system will be presented.

9:00 AM Invited

First-Principles Thermodynamic Properties of the Stable Binary B2 Phases in the Al-Ni-Ru-Ir-Pd System: *Raymundo Arroyave*[1]; Sara N. Prins[1]; Zi-Kui Liu[1]; [1]Pennsylvania State University

The B2 phases in the Al-Ni-Ru-Ir-Pd system are important for high temperature applications, especially as bond coat materials in turbine blades. To study the phase stability of these phases it is first necessary to obtain a sound thermodynamic description of the system, based on the CALPHAD method, for example. The parameters of the CALPHAD models are usually obtained through fitting of experimental data. Unfortunately, thermodynamic information on the B2 phases in this system is scarce. In this paper, we use first-principles methods to calculate the contributions of vibrational and electronic degrees of freedom to the total free energies of the stable B2 phases in this quinary system. The harmonic and quasi-harmonic approximations are used to determine the vibrational behavior of the structures, while the thermal electronic effects are taken into account through the integration of the electronic DOS.

9:30 AM

Structure, Energetics and Mechanical Stability of Fe-Cu BCC Alloy from First-Principle Calculations: *Zhe Liu*[1]; Axel van de Walle[1]; Gautam Ghosh[1]; Mark Asta[1]; [1]Northwestern University

Atomic volumes, magnetic moments, mixing energies and elastic properties of bcc Fe1-xCux solid solutions are studied by ab-initio calculations based on the cluster expansion framework. A generalization of the cluster expansion technique is developed to compute the elastic constant tensor for disordered solid solutions. Calculated mixing energies, atomic volumes and magnetic moments are found to be in good agreement with available measurements for metastable alloys prepared through non-equilibrium processing techniques. While the predicted bulk modulus and C44 in the solid solution are positive for all concentrations, C'=(C11-C12)/2 is predicted to be positive only for Cu concentrations less than 50 at%.

These results indicate that the mechanical instability of bcc Cu persists over a wide range of compositions. Implications of the present results are discussed in relation to the observed metastability of bcc Fe-Cu alloys, and the strengthening mechanism of nanoscale bcc precipitates in a bcc-Fe matrix.

9:50 AM
First Principles Study of Surface Ordering and Segregation in Pt-Rh Binary Alloys: *Koretaka Yuge*[1]; Atsuto Seko[1]; Akihide Kuwabara[1]; Humiyasu Oba[1]; Isao Tanaka[1]; [1]Kyoto University

The cluster expansion technique in conjunction with the first principles calculation have been applied in the Monte Carlo simulation to derive the equilibrium configuration of (111) surface in Pt-Rh alloys. Calculated surface composition profiles far above the bulk order-disorder transition temperature show the enrichment of Pt at top layer and Pt depleted at sublayer, which is in consistent with experimental observation in literature. At low temperatures, a completely different temperature-dependence of layer composition profile is found between $Pt_{25}Rh_{75}$ and $Pt_{50}Rh_{50}$. While Pt composition of $Pt_{25}Rh_{75}$ sublayer shows positive temperature-dependence, that of $Pt_{50}Rh_{50}$ has a local minimum at 200 K. The former is attributed to the relatively strong Rh segregation to sublayer, which induces the disruption of ordering. For the latter, sublayer-confined phase transition from $(\sqrt{3} \times \sqrt{3})R30°$order to disorder phase occurs due to the competition between segregation and ordering effects.

10:10 AM Break

10:30 AM Invited
Phase Relationships in Selected Functional Ceramics from First Principles: *Isao Tanaka*[1]; Atsuto Seko[1]; Koretaka Yuge[1]; Fumiyasu Oba[1]; Akihide Kuwabara[1]; [1]Kyoto University

In the present authors' group, phase equilibria, transitions and structure of solid solutions for a number of pseudo-binary oxides have been systematically investigated both by theory and experiments. Theoretical works have been made by first principles calculations combined with cluster expansion and cluster variation method or Monte Carlo method. Contribution of phonons has been explicitly computed using first principles lattice dynamic method within the quasi-harmonic approximations. Experimental works by x-ray absorption near edge structures technique have been made in parallel to these theoretical works. Effects of external pressure on the phase equilibria have also been investigated both by theory and experiments.

11:00 AM
First Principles Study on Pressure-Induced Phase Transition in ZnO and ZnO-MgO System: *Atsuto Seko*[1]; Fumiyasu Oba[1]; Akihide Kuwabara[1]; Isao Tanaka[1]; [1]Kyoto University

The pressure-induced phase transition from wurtzite to rocksalt in ZnO was investigated using first principles lattice dynamics calculations within the quasi-harmonic approximation. Structural and thermodynamical properties at finite temperatures were well reproduced for both phases. The transition pressure shows negative temperature dependence in consistent with previous experimental observations. This can be attributed to a greater increase in vibrational entropy of the rocksalt phase with temperature. The effect of alloying with MgO on the phase transition was also examined in conjunction with the cluster expansion and cluster variation method. The transition pressure decreases with an increase of MgO content. This behavior is due to the energetical preference of the rocksalt phase to the wurtzite phase in MgO and the increase in configurational entropy.

11:20 AM
Predicted Metastable Phase Boundaries in Al-Mg-Si from First-Principles: *Hui Zhang*[1]; Chinnappan Ravi[2]; Chris Wolverton[2]; Long-Qing Chen[1]; Zi-Kui Liu[1]; [1]Pennsylvania State University; [2]Ford Motor Company

The Al-Mg-Si system forms important alloys, in part due to their age hardening characteristics. For Al-rich alloys in this system, the metastable precipitate β" is often the most effective hardening precipitate. Knowledge about the solvus of metastable phases is critical for understanding the physical and mechanical properties of these alloys. However, due to the complexity of the precipitation sequence, the metastable phase solvus boundaries are very difficult to determine experimentally. In present work, we have obtained the formation enthalpies and vibrational entropies of the stable β (Mg2Si) phase and the metastable β' (Mg2Si) and β" (Mg5Si6) phases through first-principles total energy and frozen phonon calculations. We have then used these first-principles thermodynamic values as input to a computational thermodynamics, or CALPHAD, approach to predict the solvus boundaries of β, β', and β" for Al-rich compositions different Mg/Si ratios. In all cases, the results are compared with existing experimental results.

11:40 AM
Linear Response Theory verses Frozen Phonon Method: Ab Initio Thermodynamic Calculation: *Yi Wang*[1]; [1]Pennsylvania State University

Comparing calculations for the thermodynamic properties have been done between the linear response theory and the frozen phonon method using Al, Cu, Mg, Si, Mo, Ta, and q'-Al2Cu as the prototype. We have examined the linear thermal expansion coefficient, heat capacity, and entropy as the functions of temperature up to about melting point. We found that the results produced by the two methods are comparable.

12:00 PM
Thermodynamic Effects of Resonance Modes in Al-Ag: *Max Guy Kresch*[1]; Tabitha L. Swan-Wood[1]; Oliver Delaire[1]; Brent T. Fultz[1]; [1]California Institute of Technology

There is an unusually strong temperature dependence of the solubility of Ag in Al. Resonance modes, where heavy atoms undergo damped, low frequency vibrations, are known to exist in this system. To investigate the thermodynamic effects of these modes, we measured phonon densities of states (DoS) of Al-7 at. % Ag at 20°C (RT) and 520°C, and of elemental Al at RT. A Mannheim model showed that the resonant peak should have a large impact on the thermodynamics of the alloy. The low frequency Ag vibrations were observed in our Born von K×rm×n fit of the Al-7 at. % Ag DoS at RT, and the calculated frequencies compared favorably with experimental findings. By fitting the remaining DoS, we are able to further characterize the effects of the resonance mode on the phase stability of Al-Ag.

Deformation and Fracture from Nano to Macro: A Symposium Honoring W. W. Gerberich's 70th Birthday: Fracture, Fatigue, Wear, and Adhesion

Sponsored by: The Minerals, Metals and Materials Society, TMS Materials Processing and Manufacturing Division, TMS Structural Materials Division, TMS/ASM: Mechanical Behavior of Materials Committee, TMS: Nanomechanical Materials Behavior Committee
Program Organizers: David F. Bahr, Washington State University; James Lucas, Michigan State University; Neville R. Moody, Sandia National Laboratories

Monday AM — Room: 214D
March 13, 2006 — Location: Henry B. Gonzalez Convention Ctr.

Session Chairs: David F. Bahr, Washington State University; John M. Jungk, Sandia National Laboratories

8:30 AM Invited
Adhesion and Mechanical Behavior of Thin-Film Structures for Emerging Technologies: *Reinhold H. Dauskardt*[1]; [1]Stanford University

The mechanical behavior of materials when confined to small length scales together with their fracture and fatigue behavior effects the mechanical integrity of a wide range of thin-film device structures. Two unique challenges for emerging technologies involve the introduction of new nanostructured materials and the effect of device architecture including length-scales and aspect ratios. Materials and interfaces are nearly always optimized for other desired properties (e.g. dielectric properties, diffusion resistance, reduced carrier scattering) and the resulting effects on thermo-mechanical performance can be significant. We will present results from experiments and multiscale simulations showing the effects of interface parameters and thin-film deformation on mechanisms of debonding. Accelerated crack growth in complex chemical environments is also dis-

cussed. Implications for device reliability, integration of new materials, and life prediction are discussed.

8:50 AM

Wear-Induced Nanoscale Surface Reconstruction Patterns: *Alex A. Volinsky*[1]; Bartek Such[2]; Marek Szymonski[2]; [1]University of South Florida; [2]Jagiellonian University

The formation of surface patterns has been previously observed when scanning the surface of single crystals with an AFM tip in ultra-high vacuum. These patterns are formed of the periodic surface ripples aligned perpendicular to the scanning direction. The same experiments, but conducted in air, did not yield the same result, with a wear hole forming in the scan area. We were able to reproduce similar ripple formations by using a scanning nanoindenter in air. A KBr (001) freshly-cleaved surface was repeatedly scanned with the first ripples forming after the first several scans. We believe that there is a similarity between the nanowear-induced ripples, sand dunes and ocean-floor ripples. This paper will describe the experimental details of nanowear-induced patterns, and will try to explain the origin of surface nanostructuring and ripple formation.

9:05 AM Invited

Interfacial and Near-Interfacial Fatigue-Crack Growth: Jamie J. Kruzic[1]; Rowland M. Cannon[2]; *Robert O. Ritchie*[2]; [1]Oregon State University; [2]University of California

In this presentation, we describe the factors that affect the growth of cracks at, or near, bimaterial interfaces (primarily ceramic-metal) in micron-scale layered (sandwich) structures. For Al_2O_3/metal interfaces, cyclic fatigue-crack growth was found to occur primarily at the interface, while cracks deviated into the polycrystalline alumina for highly constrained samples at high cyclic driving forces or during overload fracture. In the presence of moisture, accelerated cracking was observed in many glass/metal and alumina/metal systems, but Al_2O_3/Al appeared to be relatively immune. Indeed, under static loading in a moist environment, interfacial crack growth was never observed at measurable rates; however, for highly constrained samples cracks did deviate off the interface and grow into the alumina, causing premature fracture. Such results are discussed in terms of the role of plastic constraint (assessed by varying the metal-layer thickness), crack path, loading mode, modulus mismatch, crack size, and the role of the environment.

9:25 AM

Properties of Wear Tested Single Crystal Nickel at the Nanoscale: *Neville Moody*[1]; Megan Cordill[2]; John Jungk[1]; Soumari Prasad[1]; William Gerberich[2]; [1]Sandia National Laboratories; [2]University of Minnesota

Strength, friction, and wear are dominant factors in the performance and reliability of nickel based LIGA devices. However, the effects of frictional contacts and wear are not well-defined. To address these effects on a fundamental level, we have begun a program using nanoscratch and nanoindentation to study wear on <001> oriented single crystal nickel. Nanoscratch techniques were used to generate wear patterns as a function of load and number of cycles. Nanoindentation was then used to measure properties in each wear pattern. The results showed a strong increase in hardness with increasing applied load but no effect of cyclic deformation, in contrast to the strong cyclic response of polycrystalline nickel. In this presentation, we will show how flow stress and plasticity evolve under sliding contacts and how these differences lead to different responses contacts in single and polycrystalline nickel. This work supported by Sandia National Laboratories under USDOE contract DE-AC04-94AL85000.

9:40 AM

Fracture Mechanics Approach to Analyzing Collapse of Micro-Contact Printing Stamps: *K. Jimmy Hsia*[1]; John Rogers[1]; Yonggang Huang[1]; Weixin Zhou[1]; [1]University of Illinois

Collapse of elastomeric elements used for pattern transfer in soft lithography is studied through experimental measurements and theoretical modeling. The objective is to identify the driving force for such collapse. Two potential driving forces, the self-weight of the stamp and the interfacial adhesion, are investigated. An idealized configuration of periodic rectangular grooves and flat punches is considered. Experimental observations demonstrate that groove collapse occurs regardless whether the gravitational force promotes or suppresses such collapse, indicating that self-weight is not the driving force. On the other hand, model predictions based on the postulation that interfacial adhesion is the driving force exhibit excellent agreement with the experimentally measured collapse behavior. The interfacial adhesion energy is also evaluated by matching an adhesion parameter in the model with the experimental data.

9:55 AM

Durability of FeCo Thin Films on Ti-6Al-4V: *Kwai S. Chan*[1]; Stephen J. Hudak[1]; Bruce R. Lanning[1]; Casey E. Smith[1]; Andrew L. Veit[1]; Glenn Light[1]; [1]Southwest Research Institute

The durability of FeCo thin films bonded on Ti-6Al-4V was studied as a function of layer thickness at ambient temperature. Interface toughness of the thin films was characterized by indentation and analyzed using an interface fracture model. The critical stresses for interface decohesion and the fatigue life response of Ti-6Al-4V with and without FeCo thin films were evaluated by three-point bend fatigue. The results indicated that the critical stress for interface debonding increased with decreasing layer thickness according to a critical energy release rate criterion. The FeCo thin films did not alter the fatigue life of the Ti-6Al-4V substrate. The presence of microcracks in the thin films did not affect the functionality of the sensor to detect strain via the inverse magneto-elastic effect. The overall durability of the films was in the range needed for practical application of the film as an imbedded sensor.

10:10 AM

Development of Adhesion Layer Dynamics for Metal Interfaces: *Marian S. Kennedy*[1]; Richard P. Vance[1]; David P. Adams[2]; Neville R. Moody[2]; David F. Bahr[1]; [1]Washington State University; [2]Sandia National Laboratories

The exact mechanism that influences the adhesion of metallic-ceramic interfaces has not been clearly identified and is generally ascribed to the mixture of several mechanisms including chemical bonding, texture, strain transfer, and plasticity. In addition, transitions between each of these mechanisms may occur during the aging process, when interlayer diffusion occurs. This study examines the combined influence of plasticity and chemical bonding with respect to the interlayer thickness and the effects of aging. The effect of film thickness was studied varying the thickness of the Ti from 0 to 17nm in a Pt/Ti/SiO2 system. Annealing heat treatments were applied to Au/SiO2 systems with a barrier layer of W to study aging kinetics. With the addition of interlayers, the toughness of the Pt/SiO2 system increased from 0.7N/m and Au/ SiO2 from 0.16N/m. Work was supported by Sandia National Laboratories under contract DE-AC04-94AL85000.

10:25 AM Break

10:45 AM

Fracture at the Nanoscale: An In-Situ Study: Julia Deneen[1]; William M. Mook[1]; Andrew M. Minor[2]; William W. Gerberich[1]; *C. Barry Carter*[1]; [1]University of Minnesota; [2]Ernest Orlando Lawrence Berkeley National Laboratory

The transmission electron microscope (TEM) is an essential characterization tool when working to bridge the gap between nanoscale and bulk mechanical behavior. Unlike traditional instrumented indentation testing methods, the TEM can discern defects, surface layers and crystal orientation at the appropriate scale. Plus, with the relatively recent development of an in-situ indentation sample holder, it is now possible not only to see a nanostructure, but also to probe it mechanically while simultaneously viewing the event in the TEM. This makes the TEM an ideal tool for investigating the deformation and failure mechanisms of individual nanoparticles. Using an in-situ indentation holder, this study investigates the mechanical response of silicon nanospheres by compressing the particles between a sapphire substrate and a diamond tip. With this approach it is possible to observe directly the dynamic processes associated with nanoscale mechanical behavior. This study presents direct evidence of plasticity-induced cleavage fracture in silicon nanoparticles.

11:05 AM

High-Cycle Fatigue in Freestanding Thin Film Metal Structures: *Maarten P. de Boer*[1]; Alex D. Corwin[1]; Paul G. Kotula[1]; Michael J. Shaw[1]; [1]Sandia National Laboratories

The elastic, plastic and interfacial properties of freestanding metal thin films are of interest in microsystems applications such as radio-frequency

devices, microrelays and optical reflectors. In this work, we have developed a new methodology to measure strength and fatigue of thin films. The test structure is an Al/0.5% Cu freestanding fixed-fixed beam of 0.5 micrometer thickness with a stress concentrating notch. We focus here on high-cycle fatigue, which is crucial in MEMS applications. Due to residual stress alone, notched structures experience plasticity. When stretched further by actuation, they unexpectedly exhibit elastic behavior until a significantly higher stress level is attained. TEM images indicate a very high dislocation density in the notched region, which is likely responsible for this strain hardening effect. When notched structures are subjected to 10 million fatigue cycles, plasticity effects are observed at much lower applied stresses. TEM then indicates striation patterns. Acknowledgment: 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.

11:20 AM

Fatigue Behavior of Freestanding Al Thin Films: *Nicholas Barbosa III*[1]; Paul A. El-Deiry[2]; Robert R. Keller[1]; Walter L. Brown[2]; Richard P. Vinci[2]; [1]National Institute of Standards and Technology; [2]Lehigh University

A test system has been developed that is capable of imposing constant total strain fatigue conditions on freestanding thin film structures 600 µm long, 100 µm wide, and 1 µm thick. Using this system, pure Al thin films have been tested under tension-tension conditions at 100 Hz with strain amplitudes from 0.08 % to 0.34 %. The Al films were found to follow a Coffin-Manson relationship with a fatigue ductility coefficient and fatigue ductility exponent of 0.022 and -0.278, respectively. Fracture morphology was similar in nature to bulk tension-tension fatigue. Slip offsets were present in the near fracture region. The behavior of the 1 µm Al freestanding films was very similar to the fatigue properties of bulk materials when the significantly smaller grain size of the films was considered. These results will be compared to work currently underway to understand the fatigue of films on substrates through an electrically-driven method.

11:35 AM

Slip Band Formation in Single Crystal Aluminum Studied by Photoelectron Emission: *Mingdong Cai*[1]; Lyle E. Levine[2]; Mark R. Stoudt[2]; J. Thomas Dickinson[1]; [1]Washington State University; [2]National Institute of Standards and Technology

We employ photoelectron emission to monitor slip band formation in single crystal aluminum (99.995%) during uniaxial tensile deformation. Deformation of single crystal aluminum with four orientations (with tensile axes near [001], [-213], [1-1-1] and [3-32], respectively) was conducted in vacuum compatible tensile stage at an initial strain rate of $1 \times 10^{-3} s^{-1}$. We show that the photoemission intensities are sensitive to changes in surface morphology accompanying deformation, including slip line and band formation. Time-resolved photoemission measurements show step-like increases in intensity consistent with the heterogeneous nucleation and growth of slip bands during tensile deformation. *In-situ* measurements of photoemission and stress versus strain for the four crystals are consistent with percolation models of dislocation motion through a pre-existing cell structure. Characterization of slip bands on the deformed surfaces was performed by optical and atomic force microscopy.

Effects of Water Vapor on High-Temperature Oxidation and Mechanical Behavior of Metallic and Ceramic Materials: Behavior of Alloys: Chromia-Formers and Low Alloy Additions

Sponsored by: The Minerals, Metals and Materials Society, ASM International, TMS Structural Materials Division, TMS/ASM: Corrosion and Environmental Effects Committee

Program Organizers: Bruce A. Pint, Oak Ridge National Laboratory; Peter Tortorelli, Oak Ridge National Laboratory; Karren More, Oak Ridge National Laboratory; Elizabeth Opila, NASA Glenn Research Center

Monday AM — Room: 213A
March 13, 2006 — Location: Henry B. Gonzalez Convention Ctr.

Session Chairs: Peter F. Tortorelli, Oak Ridge National Laboratory; Bruce A. Pint, Oak Ridge National Laboratory

8:30 AM

Thermochemistry of the CrO2(OH)2 Gas Species: *Elizabeth Opila*[1]; Nathan Jacobson[1]; Dereck Johnson[1]; Jami Olminsky[2]; Dwight Myers[3]; Mark Allendorf[4]; Ida Beck Nielsen[4]; [1]NASA Glenn Research Center; [2]QSS Group Inc; [3]East Central University; [4]Sandia National Laboratories

Chromia is known to volatilize in the presence of high temperature oxygen and water vapor to form CrO2(OH)2(g). This reaction is detrimental to chromia forming alloys in high temperature water vapor-containing environments and has been studied previously. However, there are major differences in the available thermodynamic data for the CrO2(OH)2(g) species. In this study, thermodynamic data for CrO2(OH)2(g) have been determined experimentally using the transpiration technique. In addition, thermodynamic data for this species have been calculated using high level ab initio electronic structure calculations. The experimentally determined temperature dependence as well as the oxygen and water vapor partial pressure dependence for the formation of this species are reported in comparison to the calculated data and other data available in the literature.

8:55 AM

Oxihidroxydes Analysis by TG-Mass and Thermodynamic Studies Formed on Coated and Uncoated Ferritic Steels for Supercritical Steam Turbines: *Francisco J. Perez-Trujillo*[1]; Saul Cataneda[1]; [1]Universidad Complutense de Madrid

The new supercritical steam turbines will operate at temperatures over 650°C and 300 Bar of pressure. Under those conditions the ferritic steels used upto now with chromium contents below 12% must be modificed to be creep resistant. On the other hand at 650°C, the ferritic steels are not oxidation resistant, and thus the coatings are a good altenative to extend the use of those materials. In order to analyse the behavior of the coated and coated materials a TG-Mass spectrometer with a steam loop was used and designed to perform experiments to simulate those conditions. Moreover, simulations by Thermocalc are also done to simulate the oxihidroxide formation and the solid phase formed under this conditions.Resuls of the coated and unoated materials will be shown in order to analyse the coating elements reaction with the steam.

9:20 AM

Oxidation of Alloys Targeted for Advanced Steam Turbines: *Gordon R. Holcomb*[1]; Bernard S. Covino[1]; Sophie Bullard[1]; Malgorzata Ziomek-Moroz[1]; David E. Alman[1]; [1]Albany Research Center

Ultra supercritical (USC) power plants offer the promise of higher efficiencies and lower emissions. Current goals of the U.S. Department of Energy's Advanced Power Systems Initiatives include coal generation at 60% efficiency, which would require steam temperatures of up to 760°C. This research examines the steamside oxidation of alloys for use in USC systems, with emphasis placed on applications in high- and intermediate-pressure turbines.

9:45 AM
Effect of Exhaust Gas Environment and Stress on the Mechanical Properties of Fe- and Ni-Based Alloys for Heat Exchangers: *Sebastien Dryepondt*[1]; Bruce Pint[1]; Edgar Lara-Curzio[1]; Rosa Trejo[1]; [1]Oak Ridge National Laboratory

Candidate foil (100 micrometers thickness) materials for the next generation of microturbine recuperators are being evaluated in a modified 60 kw microturbine with exhaust temperatures up to 840C. Test ports allow materials to be exposed simultaneously to the exhaust gas and an internal pressure applying a hoop stress. Cyclic exposures are performed by a pneumatic equipment designed to move similarly stressed specimens in and out of the exhaust stream. The alloy microstructure was analyzed after testing in the microturbine and miniature tensile specimens were designed to determine the evolution of tensile properties at room and high temperature as a function of the exposure duration. To establish the influence of stress and environment, other foil specimens were also tested after annealing at different temperatures, durations, and in various atmospheres such as inert gas or humid air.

10:10 AM Break

10:25 AM
Effect of Water Vapour on the Oxide Scale Growth of Chromia Forming Alloys in Low- and High-pO2 Environments: *Joanna Zurek*[1]; Michael Haensel[1]; Emmanuel Essuman[1]; Leszek Niewolak[1]; Lorenz Singheiser[1]; Willem J. Quadakkers; [1]Research Centre Juelich

The oxidation behaviour of chromia forming model alloys containing minor alloying additions of Mn and/or Ti has been studied. The test gas compositions were Ar-O2- and Ar-H2-based gas mixtures containing various amounts of water vapour. The oxidation rates were studied during isothermal exposures by thermogravimetry. Additionally, the scale growth processes were investigated in single- and two-stage oxidation tests using 18O and H218O-Tracer. The surface scale composition and morphology were analyses by light optical microscopy, scanning electron microscopy and x-ray diffraction in combination with sputtered neutrals mass spectroscopy. Main emphasis of the investigations was put on elucidating the effect of gas composition on the morphology, growth rate and adherence of the oxide scales for the various types of chromia forming alloys.

10:50 AM
Influence of Ce on the Oxidation Behavior of Fe-(9-12)Cr Steels in Moist and Dry Air: *David E. Alman*[1]; W. Keith Collins[1]; Omer N. Dogan[1]; Jeffrey A. Hawk[1]; Paul D. Jablonski[1]; [1]U.S. Department of Energy

The influence of a Ce surface treatment on oxidation behavior of a commercial (P91) and experimental steels containing 9 to 12 weight percent Cr was examined at 650C in dry and moist air. The oxidation behavior of all the alloys without the Ce modification was significantly degraded by the presence of moisture in the air (e.g., the weight gain of P91 increased by two orders of magnitude in moist air). The Ce treatment improved the oxidation resistance of the experimental steels in both moist and dry air. For instance, in moist air the Ce surface infusion treatment reduced the weight gain of a Fe-9Cr-3Co-3Cu-1Ni-0.7Mo-0.5Ti alloy by three orders of magnitude, and for comparison, was two orders of magnitude lower then P91. The Ce surface treatment did not improve the resistance of P91. The results are discussed in terms of oxide scale formation and the synergistic effects of constituent alloying elements.

11:15 AM
The Influence of Water Vapor on the Internal Oxidation of Chromium and Aluminum in Nickel Base Alloys: Frederick S. Pettit[1]; Nathan Ward[1]; *Gerald H. Meier*[1]; [1]University of Pittsburgh

Exposure of superalloys, such as Rene'-N5, as well as nickel-chromium-aluminum alloys to oxidizing conditions at temperatures from 900° to 1100°C, indicates that internal oxidation of chromium and aluminum becomes more pronounced when water vapor is present. This paper will present results on the oxidation of Ni-1(wt%)Cr and Ni-1(wt%)Al at 1000°C in air containing 10% water vapor, and in an argon-hydrogen gas mixture containing 10% water vapor. The results will be used to account for the effects of water vapor on the internal oxidation of elements in alloys.

11:40 AM
In Situ Surface Characterization of C-Mn-Si Steel during Continuous Annealing: *Tom Van De Putte*[1]; Zinedine Zermout[2]; B. C. De Cooman[1]; [1]University of Ghent; [2]Arcelor Group

High strength multi phase CMnSi steel is increasingly being used in passenger cars. Si and Mn alloying levels are typically in the range of 1-2% in mass. While Si improves the mechanical properties, it deteriorates the galvanizability of steel considerably. Residual water vapor in the reducing gas atmosphere during the intercritical annealing in a continuous hot dip galvanizing line, results in the selective oxidation of Si and Mn at the steel surface. The dew point of the furnace atmosphere is of great importance for the amount and type of surface oxidation. High dew points lead to internal oxidation and better galvanizability while low dew point values lead to the formation of external oxide films, which are the major cause of the poor galvanising. The annealing temperature also affects the surface oxidation by its influence on the ferrite and austenite phase fractions and the solubility's and diffusivities of Si, Mn and O.

Fatigue and Fracture of Traditional and Advanced Materials: A Symposium in Honor of Art McEvily's 80th Birthday: Fatigue and Fracture I

Sponsored by: The Minerals, Metals and Materials Society, TMS Structural Materials Division, TMS/ASM: Mechanical Behavior of Materials Committee
Program Organizers: Leon L. Shaw, University of Connecticut; James M. Larsen, U.S. Air Force; Peter K. Liaw, University of Tennessee; Masahiro Endo, Fukuoka University

Monday AM — Room: 216
March 13, 2006 — Location: Henry B. Gonzalez Convention Ctr.

Session Chairs: Leon L. Shaw, University of Connecticut; Robert O. Ritchie, University of California

8:30 AM Introductory Comments

8:40 AM Invited
Monotonic and Cyclic Crack-Growth Resistance in Ultrahigh-Temperature Mo-Si-B Alloys: Jamie J. Kruzic[1]; Joachim H. Schneibel[2]; *Robert O. Ritchie*[3]; [1]Oregon State University; [2]Oak Ridge National Laboratory; [3]University of California

In this presentation, the fracture toughness and fatigue-crack growth resistance of a new class of Mo-Si-B based alloys are examined from ambient to elevated (1300°C) temperatures. These alloys, which have been targeted for ultrahigh-temperature turbine engine applications, consist of an α-Mo matrix containing Mo_3Si, and Mo_5SiB_2 (T2) intermetallic phases. However, to achieve adequate resistance to oxidation, creep, fracture and fatigue, some degree of microstructural optimization is required. The role of microstructural variables including volume fraction of α-Mo, its ductility, and the morphology and coarseness of the microstructure are considered in terms of how each variable affects the observed toughening mechanisms. Primary micro-mechanisms associated with the enhancement of monotonic and cyclic crack growth have been identified as crack trapping, crack bridging, and microcrack toughening.

9:05 AM Invited
Inelastic Deformation and Its Related Life under Cyclic/Creep Loadings in Si3N4-Monolithic and Si3N4/SiCw-Composite Ceramics at Elevated Temperatures: *K. Hatanaka*[1]; Y. Ishiga[2]; R. Kawazoe[2]; M. Hasui[2]; J. Ohgi[2]; H. Ogawa[1]; [1]Ube National College of Technology; [2]Yamaguchi University

The push-pull low cycle fatigue and creep tests were performed in the monolithic- Si3N4 and the composite- Si3N4/SiCw materials at 1,300°C. Cyclic stress-strain response and creep strain were measured with newly developed extensometer. The inelastic strain, which is greatly dependent upon stress rate, was detected in both the materials. It was found that inelastic strain was easier to generate under tensile than compressive loading; the width of the hysteresis loop is larger on tensile stress side than on compressive stress side. Such a characteristic cyclic stress-strain response

is much more enhanced in the composite than in the monolithic-Si3N4. The low cycle fatigue life plotted against inelastic strain range is much longer in the former than in the latter. Moreover, the greater creep resistance is attained in the former than in the latter at the lower stress level, while converse is the case at the higher stress level.

9:30 AM Invited
Prediction of the Behavior of Small Fatigue Cracks: *Masahiro Endo*[1]; Arthur J. McEvily[2]; [1]Fukuoka University; [2]University of Connecticut

A modified linear-elastic fracture mechanics approach has been proposed and developed by Art McEvily and co-workers, by which the fatigue crack growth rates of both small cracks and large cracks can quantitatively be evaluated. This paper reviews the recent results of applications of this approach to the following fatigue problems involving the prediction of the behavior of small fatigue cracks: (1) in an examination of the use of Miner's rule in fatigue life estimation under variable amplitude loading, (2) in the prediction of the fatigue strength of components that contain initially small defects or cracks, and (3) in the prediction of the fatigue life and strength of defect-containing components subjected to multi-axial stress.

9:55 AM Break

10:10 AM Invited
Combined High Cycle/Low Cycle Fatigue Crack Growth and the Influence of LCF Overloads: *James Byrne*[1]; Rodney Hall[1]; Jian Ding[1]; [1]University of Portsmouth

The fatigue crack growth (FCG) behaviour of forged Ti-6Al-4V aeroengine disk material under the conjoint action of low cycle fatigue (LCF) and high cycle fatigue (HCF) cycles, representing a very simplified flight spectrum, has been studied at room temperature and 350C. Systematic increases in LCF overload, applied prior to the commencement of the HCF cycles, reduce the contribution of the HCF cycles to crack growth rate and increase the stress intensity range, ΔKonset, at which the HCF cycles commence to contribute to crack growth rate. The FCG prediction codes FASTRAN and AFGROW are used for both temperatures and compared with experimental results. Reasonable, conservative predictions of pure HCF ancd combined HCF/LCFcrack growth rates and of the onset for HCF activity, ΔKonset, are obtained for room temperature. However, for 350C, much less accurate predictions are obtained and an alternative twoparameter(ΔK and Kmax) approach is suggested.

10:35 AM Invited
Dislocation Crack Tip Shielding and the Paris Exponent: *Johannes Weertman*[1]; [1]Northwestern University

Fatigue crack growth by the crack tip blunting and sharpening model of Laird and Smith (Phil. Mag v.7 (1962) p. 847) and Neumann (Acta. Metall v. 22 (1974) p.1155 and p. 167) leads to the second power Paris equation (da/dN = (ΔK/G)^2 where the symbols have their usual meaning) if no appreciable dislocation crack tip shielding occurs. See Weertman Mechanics of Fatigue, AMD v. 47 (1981) p. 11 and High Cycle Fatigue of Structural Materials, TMS (1997) p.41 for a proof. In the latter publication it was suggested, but not shown quantitatively, that dislocation crack tip shielding could lead to higher exponent values in the Paris equation and lower fatigue crack growth rates. In this talk/paper I give a semiquantitative account how dislocation crack tip shielding causes a reduction in the fatigue crack growth rate and an increase in the Paris exponent.

11:00 AM Invited
Probes of Localized Fatigue Crack Tip Damage from Plasticity-Environment Interaction: *Richard P. Gangloff*[1]; Yun Jo Ro[1]; Vipul Gupta[1]; Sean R. Agnew[1]; [1]University of Virginia

Alloy development and nanomechanical models of fatigue crack propagation rate require quantitative and high resolution probes of crack tip damage. This paper reviews methods applied to precipitation hardened aluminum. Synchrotron micro-Laue X-ray diffraction tomographically determines crack wake plastic strain accumulation *vs* local microstructure, microtexture, environment, and ΔK. Combined electron backscattered diffraction and stereology establish the crystallography of faceted regions of a complex fatigue crack surface, as a function of environment and slip morphology. The method orients a several-square micron area with 3-5° uncertainty. Transmission electron microscopy measures crack crystallography, dislocation distribution, and composition of crack surface films from environmental reaction. Environmental scanning electron microscopy quantifies crack tip opening shape and surface-strain distribution, and could image crack tip damage in real time. Each method is challenged by the highly localized and gradated characteristics of the crack tip process zone, particularly for low growth rates, and the complex microstructures of technological alloys.

11:25 AM Invited
Fatigue and Cyclic Plastic Deformation of Nanostructured and Amorphous Metals and Alloys: Simon Bellemare[1]; Timothy Hanlon[2]; Ming Dao[1]; *Subra Suresh*[1]; [1]Massachusetts Instiute of Technology; [2]General Electric Company

Nanocrystalline metals and bulk metallic glasses are compared for their resistance to cyclic loading. Grains of less than 100 nm increase the total fatigue life but they impair the crack growth resistance. These results are discussed in the light of elasto-plastic properties and fracture path. It is suggested that a surface layer of nanocrystalline grains on conventional alloys could help prevent crack initiation without reducing fracture resistance. In addition to conventional fatigue testing, indenters are used to generate single and repeated scratches while monitoring the friction force and the pile-up. This approach enables the generation of large plastic strain in materials with low tensile ductility. Relationships between the scratch response and material properties have been evaluated via finite element analysis and validated experimentally. Finally, maintaining the material hardness while varying alloying and grain size enable us to isolate microstructural effects on the monotonic and cyclic plastic flow properties.

General Abstracts: Electronic, Magnetic, and Photonic Materials Division: Session I

Sponsored by: The Minerals, Metals and Materials Society, TMS Electronic, Magnetic, and Photonic Materials Division, TMS: Alloy Phases Committee, TMS: Biomaterials Committee, TMS: Chemistry and Physics of Materials Committee, TMS: Electronic Materials Committee, TMS: Electronic Packaging and Interconnection Materials Committee, TMS: Nanomaterials Committee, TMS: Superconducting and Magnetic Materials Committee, TMS: Thin Films and Interfaces Committee
Program Organizers: Sung K. Kang, IBM Corporation; Long Qing Chen, Pennsylvania State University

Monday AM — Room: 211
March 13, 2006 — Location: Henry B. Gonzalez Convention Ctr.

Session Chair: Long Qing Chen, Pennsylvania State University

8:30 AM Introductory Comments

8:35 AM
A Detailed Comparative Study of Ferroelectric Lanthanide Doped Bismuth Titanate Films Prepared by Chemical Solution Deposition and Pulsed-Laser-Ablation: *Ashish Garg*[1]; X. Hu[2]; Z. H. Barber[2]; [1]Indian Institute of Technology; [2]University of Cambridge

Thin films of ferroelectric Bi-layered Lanthanide doped bismuth titanate 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. 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 by chemical solution deposition and pulsed laser ablation. To investigate the influence of type process on the film properties, the films were grown by pulsed laser deposition (PLD) and chemical solution deposition (CSD) followed by detailed structural and ferroelectric characterization. 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.

9:00 AM

A Method for Producing Photonic Crystals with Controlled Defects: *Harris L. Marcus*[1]; Ramazon Asmatulu[1]; Sejong Kim[1]; Robin M. Bright[1]; Fotios Papadimitrakopoulos[1]; [1]University of Connecticut

This paper describes an approach to make 2D photonic crystals with controlled defects. The approach uses a dielectrophoresis cell to create the ordered polystyrene particles to create a photonic crystal. The polystyrene particles are bound to the substrate with hybridized DNA. A pulsed lased introduces defects into the crystal to create a desired defect structure. The full nature of the processing will be described. Examples of the controlled defects in the crystals will be presented. The 2D photonic crystals when fully developed have a wide range of applications in a variety of optical networks.

9:25 AM

Effect of Grain Orientation on Tantalum Erosion Rate during Magnetron Sputtering: Zhiguo Zhang[1]; Ling Kho[1]; *Charles E. Wickersham, Jr.*[1]; [1]Cabot Corporation

The differential sputter erosion rates of tantalum grains during argon ion magnetron sputtering are reported. It is well known that there is a crystallographic dependence of sputtering rate and that grains with different crystallographic orientations relative to the bombarding ion direction will sputter at different rates. This differential sputtering when coupled with the strong crystallographic texture of metallic sputtering targets is a significant factor in determining the film thickness uniformity and deposition rate for a given sputtering target. This paper provides measurements of the sputter erosion rates for grains. Electron Backscatter Diffraction (EBSD) is used to determine each grain orientation relative to the impinging argon ion. An inverse pole figure showing contour map of the variation in sputter erosion rate with grain orientation is provided. These results are also compared to the orientation effect expected from ion channeling.

9:50 AM

Electro-Deoxidation of Mixtures of Niobium Pentoxide, Titanium and Tin Oxides to Form Nbti and Nb3Sn Superconductors: *Derek J. Fray*[1]; Yong Yan[1]; [1]University of Cambridge

NbTi and Nb3Sn superconductors were synthesised directly from the oxides by electro-deoxidation where an intimate mixture of the sintered oxides was placed in a eutectic mixture of calcium chloride and sodium chloride. The oxide mixture was made the cathode and the overall cathodic reaction was the ionisation of the oxygen to form ions that dissolved in the salt and diffused to the anode where they were discharged. The cathode formed NbTi alloys and the Nb3Sn superconducting intermetallic compound which were confirmed by X-ray diffraction and their superconducting transistions.

10:15 AM Break

10:45 AM

Preparation and Electrochemical Characteristics of Sialon Bonded SiC: *Shulan Wang*[1]; Ying Yang[1]; Laan Fan[1]; [1]Northeastern University

Sialon bonded SiC was prepared by the conventional solid reaction at 1600°C and N2 atmosphere from Si3N4, Al2O3, AlN and SiC, and its A.C. impedance spectra were measured at the temperature range from 298K to 873K. There were two semicircles in the AC impedance spectra corresponding to the responses of SiC grain and grain boundary. By simulating the AC impedance spectra with equivalent circuits, conductivities of the grain and grain boundary as well as the energy intervals of SiC were obtained. The conductivity of SiC grain is much bigger than that its grain boundary, indicating Sialon mainly in the grain boundary region of the materials and bonded SiC together.

11:10 AM

Processing Novel Nanostructures by Ion Beam Mixing: *Sufian Abedrabbo*[1]; Dia-Eddin Arafah[1]; Ravi Ravindra[2]; [1]University of Jordan; [2]New Jersey Institute of Technology

Special nanostructures are processed utilizing the technique of Ion Beam Mixing (IBM). One example is GeO2 nano-dimensional films that are formed by annealing following the IBM. Other examples include fabrication of silicon on oxides and nitrides (SOI). Characterization processes include investigations of the structural variations noted due to Argon beam irradiation to various fluences by Rutherford Backscattering (RBS), shallow defects and deep trapping level states by Thermo luminescence (TL), X-ray Diffraction (XRD) are performed.

11:35 AM

Electro-Catalyzed Metallorganic Chemical Vapor Deposition of Copper Films: *Yu-Lin Kuo*[1]; Chiapyng Lee[1]; Kou-Liang Liu[1]; Yee-Wen Yen[1]; [1]National Taiwan University of Science and Technology

This study investigated a novel technique of metallorganic chemical vapor deposition (MOCVD) of copper thin films on TaN/Si substrates using (hfac)Cu(COD) as precursor. Owing to the lower nucleation density of Cu(I) complex used in the traditional Cu-MOCVD process, we proposed a new idea of electro-catalyzed Cu-MOCVD process by supplying direct current to TaN/Si substrates. Our results revealed that supplying direct current to TaN/Si substrates not only helps to reduce the Cu incubation time but also significantly enhances Cu nucleus density and reduces Cu nucleus size. In the traditional Cu-MOCVD process without supplying direct current, activation energy (Ea) values of mass-transfer limited and surface-reaction limited regions were 1.28 Kcal/mol and 19.33 Kcal/mol, respectively. Introducing direct current to the Cu-MOCVD process apparently reduced the activation energy of surface-reaction limited region to 7.90 Kcal/mole. The proposed electro-catalysis Cu-MOCVD process was found to succeed in forming smooth and continuous thin copper films.

12:00 PM

A Computational Model to Simulate the SIMOX Process: *Sergio D. Felicelli*[1]; Supapan Seraphin[2]; David Robert Poirier[2]; [1]Mississippi State University; [2]University of Arizona

A finite element model was developed to simulate the production of silicon-on-insulator substrates through the technique known as SIMOX (Separation by IMplantation of Oxygen). The simulation initiates from an as-implanted distribution of SiO2 precipitates and calculates the time evolution during constant temperature annealing of the number, size, and shape of precipitates. Under proper process conditions, the redistribution of precipitates can lead to the desired formation of a buried oxide layer under a surface-silicon layer. During the evolution, the precipitates grow, dissolve, merge, or split, and can adopt arbitrary shapes under the dynamic interaction of the oxygen concentration diffusion and capillary forces. The simulations show that the model reproduces several phenomena observed during the SIMOX process, like Ostwald ripening and the formation of silicon islands. Results compare qualitatively well with actual TEM images of annealed SIMOX layers.

General Abstracts: Extraction and Processing Division: Lead and Other Metals

Sponsored by: The Minerals, Metals and Materials Society, TMS Extraction and Processing Division, TMS: Aqueous Processing Committee, TMS: Copper and Nickel and Cobalt Committee, TMS: Lead and Zinc Committee, TMS: Precious Metals Committee, TMS: Process Fundamentals Committee, TMS: Process Modeling Analysis and Control Committee, TMS: Pyrometallurgy Committee, TMS: Recycling Committee, TMS: Waste Treatment and Minimization Committee, TMS: Materials Characterization Committee
Program Organizers: Thomas P. Battle, DuPont Company; Michael L. Free, University of Utah; Boyd R. Davis, Kingston Process Metallurgy

Monday AM — Room: 207A
March 13, 2006 — Location: Henry B. Gonzalez Convention Ctr.

Session Chair: Boyd R. Davis, Kingston Process Metallurgy

8:30 AM
Improving Metallurgical Operations through the Application of Systems Thinking Principles: *K. Narayana Swamy*[1]; [1]Doe Run Company

The traditional approach to improving the operating efficiency of a metallurgical plant has been to study individual unit operations and focus on improving the poor-performing unit operations. The complex nature of most metallurgical plants call for a holistic approach that will consider the whole rather than just focus on the individual units of a plant. This holistic approach is part of the systems thinking principles. Numerous case studies highlight the importance of the need to apply systems thinking principles in improving the effectiveness of metallurgical operations. Improving the efficiency of one unit operation without considering its effect on the performance of other unit operations has in many cases lead to lower overall operational efficiency. Modelling and simulation are key to the application of the systems thinking principles. Standard flowsheet models are very useful in scenario analyses though they have to be supplemented with other models for useful predictions.

8:55 AM
Cathodic Refining of Metals in Molten Salts: *Derek J. Fray*[1]; George Z. Chen[2]; [1]University of Cambridge; [2]University of Nottingham

The removal of non-metallic impurities, including oxygen, sulphur and selenium, from molten metals was achieved by making the molten metal the cathode in a bath of molten calcium chloride. On the application of a cathodic potential to the metal, the non-metallic impurities ionised and dissolved in the salt and were subsequently discharged at the anode. The form of the ionisation reaction was O + 2e = O2- In order to increase the mass transfer of the impurities a novel recessed electrode was used. The results demonstrated the usefulness of this approach in terms of space, time and yield of product and offering considerable advantages over a simple electrorefining cell.

9:20 AM
Application of Transformational Roasting to the Treatment of Metallurgical Wastes: *Preston C. Holloway*[1]; Thomas H. Etsell[1]; [1]University of Alberta

Transformational roasting involves the heating of a material to high temperatures along with specific additives to induce mineralogical changes in the starting material. By controlling the chemical composition, roasting atmosphere, temperature and time of reaction, the mineral transformations induced during roasting can be engineered to control the distribution of valuable, or harmful, metals and to produce new mineral assemblages that are more amenable to conventional methods of metals recovery or to environmentally safe disposal. To date, commercial application of this type of process has been limited to the recovery of Cr, Li, V and Zr, but current research is looking to expand the application of these techniques to the recovery of a wider range of metals. An introduction to these techniques is presented along with preliminary results from their application to metals recovery from metallurgical wastes, such as zinc ferrite residues and electric arc furnace dust.

9:45 AM Break

10:05 AM
Reaction Mechanism of the Alumino-Thermic Reduction of Metal Oxide and Its Application to Hot Metal Pretreatment: *Mamoru Kuwabara*[1]; Jian Yang[1]; Takashi Asano[1]; Masamichi Sano[1]; [1]Nagoya University

Reaction mechanism of the alumino-thermic reduction of metal oxide in a compact pellet is investigated using a high temperature microscope coupled with SEM observation and EDX analyses. Nano-sized alumina film covering each aluminum powder even at room temperature is further thickend during heating the compact. No alumino-thermic reduction is found to take place until a limiting temperature around 1150°C. When the pellet is heated above the temperature, a great many cracks are formed on the alumina film due to thermal shock, and liquid aluminum coming out through the cracks penetrates into the surrounding metal oxide powder phase to react with. Thus, the initial stage of the reaction mechanism is not governed by a chemical reaction characterized by Arrhenius equation. Typical applications of this alumino-thermic reduction of metal oxides to the ironmaking processes are exemplified to give better insights into improvement of desulphurization operation and low temperature slag formation.

10:30 AM
Thermodynamic Modeling of Copper Drossing Process in Lead Refining: *Pengfu Tan*[1]; Pierre Vix[1]; [1]Xstrata Copper

Lead blast-furnace bullion cooled to near its freezing point in an operation known as copper drossing or hot drossing usually contains 0.02-0.06% copper. The removal of this copper is usually carried out in a batch operation known as sulphur drossing. Sulphur is stirred into the bullion at temperatures near its freezing point, and the dross of copper and lead sulphides that floats to the surface is skimmed off manually. A thermodynamic model has been developed to simulate the copper drossing. The phase diagram of Pb-Cu-S system has been calculated, and the effects of the process parameters, such as temperature, copper content, and sulphur content, on the drossing process have been simulated and discussed.

10:55 AM
Thermodynamic Modeling of Kivcet Lead Process: *Pengfu Tan*[1]; Pierre Vix[1]; [1]Xstrata Copper

A thermodynamic model has been developed to predict the distribution behavior of Pb, Zn, Fe, S, O, As, and heat balance in Kivcet direct lead smelting furnace. The compositions of lead bullion, matte, slag and gaseous phases, and heat balance are calculated. The model predictions were compared with the known industrial data from Portovesme Company, and an excellent agreement was obtained. The effects of oxygen, coke, smelting temperature, and temperature of coke checker on the heat balance and furnace control have been discussed. In this paper, the applications of this model have been presented.

Granulation of Molten Materials: Session I

Sponsored by: The Minerals, Metals and Materials Society, TMS Extraction and Processing Division, TMS: Copper and Nickel and Cobalt Committee, TMS: Lead and Zinc Committee, TMS: Pyrometallurgy Committee
Program Organizers: Cameron L. Harris, HG Engineering Ltd; Hani Henein, University of Alberta

Monday AM — Room: 7C
March 13, 2006 — Location: Henry B. Gonzalez Convention Ctr.

Session Chair: Phillip Mackey, Falconbridge

8:30 AM Introductory Comments by Phillip Mackey

8:35 AM
Granulation of Molten Materials: *David Norval*[1]; [1]Bateman Engineering

Water solidification of mattes, metals, alloys and certain slags with high metal entrainment has customarily not been practiced due to the be-

lief that such processes are too dangerous and unproven in the Pyrometallurgical Industry. Slag granulation on the other hand is extensively applied, although in some cases crudely with disastrous effects as a result of not recognising the high heat capacities prevalent in slags. This paper will examine the most common air solidification processes and compare such processes with water solidification, mainly slag and matte granulation processes and design criteria for safe and reliable operation. Finally, purpose designed granulation and solidification processes will be discussed taking into account specific applications and the individual signatures of alloys and slags, emphasising that no slag, matte or alloy responds in similar fashion to a granulation practice.

9:00 AM
Evolution of Granulation Technology: *Bob Greiveldinger*[1]; [1]Paul Wurth S.A.

Encouraged by a strongly growing and evolving market for granulated products, Paul Wurth continuously improved its granulation and dewatering technologies to provide customers with state of the art installations. Continuously developed know-how about the granulation process of iron blast furnace slag enabled application to non-ferrous materials such as Ni-Slag, Pb-Slag, Blister Copper, Cu-Matte and even TiO2-Slag, which rank among the most difficult materials to granulate. This paper identifies how critical objectives in granulation and dewatering technologies applied to different molten materials with respect to various product quality objectives can be addressed. The differences between hot and cold water granulation systems are explained, including the step from cold runner to granulation water tank. Development of a flow and pressure controlled blowing box is the latest step to optimize the granulation process in order to meet the latest standards in terms of quality, power consumption and environmental protection.

9:25 AM
Common Granulation Systems in the Metals Industry: *Art Cooper*[1]; [1]Carlingview Technologies Ltd.

Granulation systems are common in the metals industry. The process of granulating slags, mattes and metals is more than a century old, and a number of different systems have been developed to accomplish this task. These systems have followed an evolutionary path, and may be characterized by common elements in terms of molten material handling, granulationmethods and post-granulation processing. This paper will summarize the more common systems used in the metals industry, with particular reference to non-ferrous applications.

9:50 AM Break

10:15 AM
Copper Matte Granulation at the Kennecott Utah Copper Smelter: *David B. George*[1]; David George-Kennedy[2]; Colin Nexhip[1]; Robert Foster[2]; [1]Rio Tinto Technology Services; [2]Kennecott Utah Copper

Kennecott Utah Copper adopted Flash Smelting and Flash Converting in 1995, a process based on granulating high grade copper matte. While nickel mattes and small quantities of copper matte had been commercially granulated for years, no large scale copper matte granulation system had been built. This paper summarizes the history and benefits of copper matte granulation, the Kennecott design basis, the successful operation for over 10 years and potential problems inherent in some matte granulation approaches.

10:40 AM
Granulation of Precious Metal-Bearing Alloys and Slags: *William Kelly O'Connor*[1]; Paul C. Turner[1]; [1]U.S. Department of Energy

A molten metal granulator was designed and fabricated at the U.S. Dept. of Energy, Albany Research Center, for granulation of precious metal-bearing alloys and slags. The system was designed to safely granulate a metal alloy at a temperature of up to 1,600°C at a rate of roughly 100 lb of alloy per minute. The primary water jet was supplied by a 25-hp, 160 gpm pump which provided approximately 1,200 lb of water per minute through the primary jet. Two 5-hp, 80 gpm auxiliary pumps provided additional wash water to wet the granulation trough through 4 secondary jets, which were placed at either side of the primary jet. The water supply was closed-loop, including a 10,000-gallon supply tank and 6,000-gallon recovery tank. Magnetic separators and particulate filters were included for collection of the finest fraction of the granulation product, which cleaned the water sufficiently for continuous recycle.

11:05 AM
Multimedia Dispersion and Solidification of Molten Material Flows: *David Arana*[1]; Hendrik LeRoux[2]; Art Cooper[3]; [1]Vidabrazil; [2]Read, Swatman & Voigt Ltd.; [3]Carlingview Technologies Ltd.

The use of gas-water dispersion of a molten material flow onto a vibrating surface is developed as a process to minimize water pumping requirements, minimize the risks of explosions, and minimize the post solidification dewatering and fines handling equipment requirements. The process uses existing vibration transport technologies and common plant utilities. Plant trials using the smaller footprint and the progressive molten particle cooling time have yielded encouraging results. The results are analyzed and reported.

11:30 AM
Properties and Uses of Granulated Non-Ferrous Slag: *Michael P. Sudbury*[1]; Denis J. Kemp[2]; [1]Michael P. Sudbury Consulting Services Inc; [2]Falconbridge Ltd

Non-ferrous slags are granulated and stockpiled as an alternative to pit cooling or transporting molten slag to a dump. The chemical composition of such slag is determined by the pyrometallurgical process in which it is produced, while the size distribution is set by safety concerns or a desire to reduce wear of pumps, pipelines and other equipment. Relatively few operations give consideration to the effect of granulation conditions on other properties of the granulate as the material is typically accumulated on the smelter site. It is becoming recognized that slag has many potential commercial uses and carries much of the energy applied to the smelting operation. This paper outlines the findings of extensive work to identify uses forgranulated non-ferrous slag, the importance of preparation conditions on the properties, impediments to more extensive use of granulated slag, the real costs of slag stockpiling and the opportunities for further productive research.

11:55 AM Concluding Comments by Cam Harris

Lead Free Solder Implementation: Reliability, Alloy Development, and New Technology: Mechanical Behavior I: Thermal Fatigue, Shock, and Reliability

Sponsored by: The Minerals, Metals and Materials Society, TMS Electronic, Magnetic, and Photonic Materials Division, TMS: Electronic Packaging and Interconnection Materials Committee
Program Organizers: Nikhilesh Chawla, Arizona State University; Srinivas Chada, Medtronic; Sung K. Kang, IBM Corporation; Kwang-Lung Lin, National Cheng Kung University; James Lucas, Michigan State University; Laura J. Turbini, University of Toronto

Monday AM — Room: 214A
March 13, 2006 — Location: Henry B. Gonzalez Convention Ctr.

Session Chairs: Srinivas Chada, Medtronic; Nikhilesh Chawla, Arizona State University

8:30 AM Invited
Shock-Resistance of SnAgCu Solders: Effects of Ag and Doping: *Dave Daewoong Suh*[1]; Heeman Choe[1]; Mitesh Patel[1]; Tiffany Byrne[1]; Ted Martin[1]; Ashay Dani[1]; [1]Intel Corporation

Current industry standard near-eutectic SnAgCu (SAC405/305) alloys are significantly worse than eutectic SnPb in terms of their shock performance. In this article, effects of Ag and doping elements on shock-resistance of SnAgCu alloys are presented. Technical strategy for bulk and interface optimization is derived from the understanding of shock damage process. For bulk optimization, elastic compliance is identified as a key property and metallurgical simulation/technique to achieve enhanced bulk compliance is presented. It is shown that by optimizing the content of Ag (which does not participate in interfacial reaction), considerable bulk compliance can be achieved and shock performance is accordingly

improved. Effects of optimum Ag content on other relevant properties and performance is also examined. Interface optimization strategy through doping is presented for representative surface finishes. Representative data on doping element effects on interfacial reaction and resultant interface characteristics are presented. The resultant interface characteristics are correlated with drop/shock performance.

8:55 AM

Thermal Fatigue of Pb-Free Solders: Experiments and Microstructure-Based Simulation: *Rajen S. Sidhu*[1]; Nikhilesh Chawla[1]; [1]Arizona State University

Pb-free solders encounter several mechanical and thermal loading conditions in service. In particular, thermal fatigue is extremely important. In this presentation, the thermal fatigue behavior of individual solder spheres, reflowed on Cu substrates, will be discussed. Sn-Ag, Sn-Cu, Sn-Ag-Cu and pure Sn solder spheres, 1 mm in diameter, were reflowed onto copper substrates to form lap shear specimens and thermal cycling was conducted. The specimens were cycled through the temperature range between -20°C and 130°C. Microstructure evolution during thermal fatigue damage was characterized. By correlating the microstructure with cycles to failure, the underlying mechanisms for deformation during thermal fatigue of Sn-rich solders was elucidated. To further understand the crack growth behavior within these complex solder microstructures, we have used a two-dimensional finite-element approach to understand the effects of: (a) Ag_3Sn particle size and distribution and (b) Cu_6Sn_5 layer morphology and thickness on shear deformation and damage development during thermal fatigue.

9:15 AM

Fatigue Test for Determining the Cyclic Stress-Strain Response of Solder Joints Connecting Rectangular Components to Circuit Boards: *Raymond A. Fournelle*[1]; Paul B. Crosbie[2]; [1]Marquette University; [2]Motorola

A new test for analyzing the low cycle fatigue experienced by solder joints on a circuit board has been developed. This test simulates the strains that a solder joint experiences during thermal cycling by mechanically cycling tensile specimens made of fiberglass circuit board with rectangular copper "components" soldered to them. The mismatch between the elastic moduli of the fiberglass and the copper generates strains in the solder joints when the fiberglass specimen is load cycled. The test involves direct measurements of the load in the fiberglass specimen and the tensile strain in the surface of the rectangular copper component. Using an approximate analytical analysis based on a two dimensional FEA model, these measurements are converted into average stresses and strains in the solder joints. Cyclic stress-strain hysteresis loops obtained for a Sn-Ag-Cu alloy exhibit good agreement with those reported in the literature. The joints also cyclically soften during cycling.

9:35 AM

Mechanistic Reliability Model for Thermo-Mechanically Driven Thin Film Delamination in Microelectronic Packages: *Shubhada Sahasrabudhe*[1]; Arun Raman[1]; Xuejun Fan[1]; Mukul Renavikar[1]; Alan Lucero[1]; Sandeep Sane[1]; [1]Intel Corporation

While performing reliability predictions, typically a generic reliability model is used across different microelectronic package failure mechanisms and the physics of failure is rarely tied to the model. This paper presents a science based reliability model developed for a typical thin film delamination mechanism in microelectronic packages that occurs under thermo-mechanical stress. High temperature exposure causes intermetallic compound growth at metal interfaces, inducing Kirkendall voids eventually leading to thin film delamination. Mechanistic understanding will be offered by linking phenomenological observations to key reliability model parameters. During model validation, the predicted failures matched remarkably within 5% of the experimental results. The paper includes elaborate sequential stress testing, intense failure analysis, detailed finite element simulation and complete statistical analysis.

9:55 AM

Critical Void Size and Location on Lead-Free Solder Joint Reliability: *De-Shin Liu*[1]; Bo-Kuan Lin[1]; Cho-Liang Chung[1]; [1]National Chung Cheng University

Voiding occurred in lead-free solder joint due to improper reflow profile and unfit flux system is one of the major failure modes to reduce the solder reliability. However, small voids can act as stress relievers and also can changing the crack pattern to maintain sufficient life cycles. In order to understand the effects of voids on the lead-free package performance, mini-BGA packages with Sn-3.5Ag-0.5Cu solder are used to undergo the temperature cycling test (TCT) with different IR-reflow peak temperatures to examine the void forming mechanism and compared life cycles. A three dimensional finite element (FE) model of mini-BGA was built and analyzed with relative constitutive equations. Analysis results are shown that the critical void size is about one-eighteenth of solder diameter. Higher stress level can be found as the void location closed to solder bonder.

10:15 AM Break

10:30 AM

Material Optimization and Reliability Characterization of Indium Solder Thermal Interface Material for CPU Package Technology: *Carl L. Deppisch*[1]; Arun Raman[1]; Fay Hua[1]; Thomas Fitzgerald[1]; Mikel Miller[1]; Charles Zhang[1]; [1]Intel Corporation

Developing new thermal interface materials (TIM) is a key activity to meet package thermal performance requirements for future generations of microprocessors. Indium solder is capable of demonstrating end of line (EOL) performance to meet current targets due to its inherent high thermal conductivity. However, improving its reliability performance, particularly in temperature cycling, proved to be challenging. This study describes the failure mechanisms and reliability performance of indium solder TIM as a function of integrated heat spreader (IHS) metallization thickness, TIM bond line thickness and die size and the steps taken to improve its temperature cycle performance. Analyses were performed using thermal resistance measurement (TRES), scanning electron microscopy (SEM), scanning acoustic microscopy (SAM) and transmission electron microscopy (TEM) to characterize the solder TIM thermal performance, interfacial microstructure and failure mechanisms.

10:50 AM

Thermal Shock Behavior of Sn-3.5Ag Solder Joints at Various Temperature Extremes and Number of Cycles: Bo Li[1]; *Fu Guo*[1]; Andre Lee[2]; K. N. Subramanian[2]; [1]Beijing University of Technology; [2]Michigan State University

There has been increasing number of microstructural and mechanical studies on the thermomechanical fatigue (TMF) behavior of Sn-3.5Ag solder in the joint configuration. However, the TMF behavior of such solder joint and its effect on the residual mechanical properties have not been reported in a systematic manner. In the current research, thermal shock experiment on eutectic Sn-3.5Ag solder joint are carried out at various number of cycles and temperature extremes. Mechanical properties such as shear stress, peak shear stress are evaluated as a function of different temperature extremes, and number of cycles to gain a better understanding of the parameters contributing to thermomechanical fatigue or thermal shock resistance of Sn-3.5Ag solder joint.

11:10 AM

Probabilistic Microstructure Based Approach for Reliability Analysis of Lead-Free Solders: *Ganapathi Krishnan*[1]; Robert G. Tryon[1]; Robert J. Matthews[1]; [1]Vextec Corporation

Reliability of solder interconnects is of prime concern in the transition from lead to lead free solders. Seventy percent of failures in microelectronic components have been attributed to interconnects, therefore accelerated evaluation of reliability a new lead-free solder alloys is needed to save developmental costs and time. Microstructure based damage models developed by VEXTEC Corporation provide the tools needed to evaluate the performance of solder under operating conditions with limited experimental data. This paper presents the methodology developed to evaluate lead-free solder alloys based on models developed for eutectic Sn/Pb solders. The performance of the solder alloy and a solder joint on a PCB under different board configurations and operating conditions can be evaluated.

11:30 AM

Nucleation and Propagation of Fatigue Damage in Near-Eutectic Sn-Ag-Cu Alloy: *Tia-Marie K. Korhonen*[1]; Donald W. Henderson[2]; Matt Korhonen[1]; [1]Cornell University; [2]IBM Corporation

During thermomechanical cycling, solder joint fatigue process is characterized by recrystallization of Sn grains. Grain boundary sliding and increased grain boundary damage then results in intergranular crack initiation and propagation along the recrystallized grain boundaries. In this work, fatigue tests were used to study the initial stages of deformation in SnAgCu samples. To separate solder properties from constraints introduced by the substrate, free-standing solder specimens were used. The test samples were cast dog-bone specimens with a cross section of 1mm, which corresponds to typical solder joint diameter in ball grid arrays. The solder was heated to 245 degrees, held for ten minutes, cast and cooled at 1 degree/second. Mechanical cycling was performed isothermally at several temperatures, up to 125C. Typical test conditions were 0.5% strain and 30 minute cycles. Optical microscopy, SEM, and electron back-scatter diffraction were used to study the microstructures of the samples before and after fatigue testing.

11:50 AM

Thermomechanical Response of a Lead-Free Solder Reinforced with Shape Memory Alloy: *Bhaskar S. Majumdar*[1]; L. Yang[1]; S. Ma[2]; Indranath Dutta[2]; [1]New Mexico Tech; [2]Naval Postgraduate School

In order to improve thermomechanical fatigue (TMF) life of lead-free solders, we have experimented with a NiTi shape memory alloy as a reinforcing phase. The conceptual framework is that the transformation of martensite into austenite at an elevated temperature would induce a backstress on the solder, through a transformation induced eigenstrain. This would reduce the overall creep strain of the solder. In this presentation, we extend our previous work to include the fabrication of Sn-3Ag solders reinforced with multiple fibers and particulates under transverse shear. Processing of such composites pose substantial challenges and are discussed. TMF tests were conducted on the solders, both with and without reinforcements, and the local displacement measurements are compared with results from Eshelby and finite element analysis. Transition of the methodology to actual ball grid arrays will be discussed. We acknowledge support by the Army Research Office with Dr. David Stepp as the program monitor.

Magnesium Technology 2006: Corrosion and Coatings

Sponsored by: International Magnesium Association, TMS Light Metals Division, TMS: Magnesium Committee
Program Organizers: Alan A. Luo, General Motors Corporation; Neale R. Neelameggham, US Magnesium LLC; Randy S. Beals, DaimlerChrysler Corporation

Monday AM — Room: 6B
March 13, 2006 — Location: Henry B. Gonzalez Convention Ctr.

Session Chairs: Eric A. Nyberg, Pacific Northwest National Laboratory; En-Hou Han, Chinese Academy of Sciences

8:30 AM

Conversion Coating Treatment for AZ31 Alloy in a Permanganate–Phosphate Solution: Xichang Shi[1]; George Jarjoura[2]; *Georges J. Kipouros*[2]; [1]Central South University; [2]Dalhousie University

One of the major drawbacks to using magnesium parts in automotive application is its poor corrosion resistance. Various techniques have been used to address this concern. The purpose of this work was to produce a conversion coating on AZ31 alloy. This was accomplished using a bath which contained 20g/L $KMnO_4$, 60g/L $Na_2HPO_4.7H_2O$, and 25mL/L HNO_3. The optimum conditions for the coating process were a temperature of 50°C and a time of 30 min. A conversion coating of 10 µm thickness was obtained, which was subsequently sealed in a 10g/L sodium silicate bath at 85°C for 10 min. The morphology of the conversion-coated layer was studied using SEM. The crystal structure and the composition were examined by XRD and EDS. The corrosion behaviour of the conversion coating with and without sealant was studied using potentiodynamic polarization in a 0.5M NaCl solution. The results show that the corrosion resistance improved.

8:50 AM

Corrosion and Protection of Magnesium Alloy AZ91 by a New Electroless Nickel Plating Technique: *Zhenmin Liu*[1]; Wei Gao[1]; [1]University of Auckland

A plasma electrolytic oxidation (PEO) pretreatment and electroless nickel (EN) plating were applied to AZ91 alloy to improve its corrosion resistance. By PEO pretreatment the corrosion resistance of the alloy was improved to some extent as verified by salt fog spray and potentiodynamic polarization test. A nickel coating was deposited on the PEO pretreated AZ91 alloy. The presence of the PEO film between the nickel plating and the substrate acted as effective barrier layer between them and hence enhanced the corrosion resistance of the alloy. This new EN plating technique was also compared with a traditional EN processing. It was found the polarization current density decreased by almost two orders of magnitudes under the same experimental condition. Neutral salt spray testing further demonstrated that the corrosion property of the new EN plating on AZ91 was improved significantly. More importantly, the new technique is much more environmentally friendly processing.

9:10 AM

Corrosion Behavior and Microstructure of a Broad Range of Mg-Sn-X Alloys: Tarek Abu Leil[1]; *Kamineni P. Rao*[2]; Norbert Hort[1]; Carsten Blawert[1]; Karl Ulrich Kainer[1]; [1]GKSS Research Centre; [2]City University of Hong Kong

To launch a new class of magnesium alloys based on the Mg-Sn system and to achieve a adequate combination of mechanical properties and corrosion behavior Mg-Sn alloys with additional elements like Calcium, Silicon, Strontium and Manganese have been investigated in as-cast condition in regard to their microstructure. The corrosion behavior has been investigated by means of salt spray tests and potentiodynamic measurements, accompanied by creep tests. As the microstructure of Magnesium alloys is significantly influenced by the heat treatment, different heat treated conditions were investigated additionally: I) as-cast, II) solution heating followed by quenching in water (T4),III) solution heated and then cooled inside the furnace "naturally" and IV) solution heated and aged (T6). Scanning Electron Microscopy (SEM) as well as EDX were also used to study and analyse the microstructure.

9:30 AM

Corrosion Behaviors of Polyaniline Electrodeposited on AZ91 Magnesium Alloys in Alkaline Solutions: *Y. F. Jiang*[1]; Y. G. Wu[1]; C. Q. Zhai[2]; [1]Hehai University; [2]Shanghai Jiaotong University

Polyaniline coatings deposited on AZ91 magnesium alloys with potentiodynamic methods are investigated by auger electron spectroscopy (AES) and scanning electron microscopy (SEM). Low conductivity and many microporous are showed in polyaniline coatings, and its chemical compositions are varied in different positions. The anti-corrosion of AZ91 magnesium alloys improves with polyaniline coatings.

9:50 AM

Electroless Nickel-Phosphorus Plating on AZ31 Magnesium Alloy Pretreated with a Chemical Conversion Coating: Xichang Shi[1]; George Jarjoura[2]; *Georges J. Kipouros*[2]; [1]Central South University; [2]Dalhousie University

To further improve the erosion resistance and hardness of conversion coatings on AZ31 samples an electroless nickel-phosphorus layer was successfully deposited on the chemical conversion pre-treated AZ31 alloy. The electroless bath contained nickel sulphate and sodium hypophosphite as main salts and the samples were activated in a 5g/L $AgNO_3$ solution prior to plating. The presence of the conversion coating between the nickel-phosphorus coating and the AZ31 substrate acted as a barrier and prevented corrosion of the alloy. The morphology of the nickel-phosphorus layer was studied using SEM. The crystal structure and composition were examined by XRD and EDS and the hardness was measured. The corrosion behaviour of the nickel-phosphorus layer deposited on the conversion coating was studied using potentiodynamic polarization in a 0.5M NaCl solution using a saturated standard calomel electrode as a reference

electrode. Results show that the nickel-phosphorus coatings had a significantly better corrosion resistance than the AZ31.

10:10 AM Break

10:25 AM
Nano-ZrO2 Improved Electroless Ni-P Composite Coating on AZ91D Magnesium Alloy: *En-Hou Han*[1]; Yingwei Song[1]; Dayong Shan[1]; [1]Chinese Academy of Sciences

Nanometer ZrO2 was added into the Ni-P coating on AZ91D magnesium alloy. The coating was compact, uniform and pore free, and its average chemical composition was 86.9Ni-7.9P-5.2ZrO2 (wt%). The open circuit potential measuration, potentiodynamic polarization curves, salt spray and immersion tests were carried out to understand corrosion properties of the coating. In different corrosion electrolytes of 3.5%NaCl, 1.0N NaOH and 1.0N NaSO4, electrochemical experiments showed that the corrosion resistance of Ni-P-ZrO2 composite coating was superior to that of the traditional Ni-P coating. The salt spray results showed taht the time for first corrosion pit in the nano-composite coating were doubled comparing with Ni-P coating. However, the immersion weight loss rate of the nano-composite coating was higher than that of Ni-P coating. The former is general corrosion and the later is pitting corrosion. The possible mechanisms were discussed.

10:45 AM
Sacrificial Magnesium Film Anode for Cathodic Protection of Die Casting AZ91D Alloy: *Bing Lung Yu*[1]; Jun-Yen Uan[1]; [1]National Chung Hsing University

The coatings on magnesium alloy usually act as a corrosion barrier to the environment. However, the coating must be crack free for applications otherwise the substrate material under the crack becomes local anode, leading to severe local corrosion. In present study, magnesium film was deposited on AZ91D specimen, acting as a sacrificial anode. The corrosion properties of the Mg-film coated specimen were estimated by electrochemical polarization experiments and constant immersion tests, both in 3.5% NaCl solution. The Ecorr values of the coated specimens were -1.7~ -1.66V (AgCl), which was evidently lower than that of the substrate material (AZ91D diecast specimen). According to the electrochemical analyses, the magnesium film could be used as a distributed sacrificial anode, cathodically protecting the substrate (AZ91D diecast specimen). Immersion tests showed that the uncoated specimen was severely corroded while the Mg film-coated specimen was well protected by the sacrificial anode of the magnesium film.

11:05 AM
Selected Etching Surface Treatment for Improving the Corrosion Resistance of Die Cast AZ91D Thin Plate: *Ching Fei Li*[1]; Jun-Yen Uan[1]; [1]National Chung Hsing University

HF-H2SO4/CaCO3 surface treatment was explored in present study. This selected etching treatment attempted to remove the most corroding phase in the die skin of AZ91D thin plate, but left the rest of the die skin structure behind. It was found that Al-rich-a phase (eutectic a) was the most corroding phase, which located at interdendritic spacing. The Icorr value of the HF-H2SO4/CaCO3 - treated specimens were approximately ~5 μA/cm2, significantly lower than that of the as-diecast AZ91D (~ 300 μA/cm2). The purpose of the CaCO3 application was to decrease the fluorine left on the treated specimen surface. The selected etching treatment also resulted in the opening structures that were distributed all over the sample surface. The opening structure could provide good adhesion between the metallic substrate and the protective paint. The etching treatment explored in present study not only improved corrosion performance but also left no fluorine remained on the surface.

11:25 AM
Corrosion Behaviour of Electroless Nickel Plating on AZ91 Mg Alloy: *Zhenmin Liu*[1]; Wei Zhang[1]; Alec Asadov[1]; Wei Gao[1]; [1]University of Auckland

AZ91 Mg alloy was electroless plated with nickel-phosphorous (Ni-P) coating containing 2.3 - 12.6 wt.% P. Salt fog spray testing and anodic polarisation were used to study the effects of P, coating thickness and microstructure on the corrosion behaviour. It was found that micro-cracks exist within the high P containing Ni plating (12.6 wt. % P), causing galvanic corrosion. Corrosion potential and current density were obtained from polarisation curves measured in an aerated 3.5%NaCl solution. The results indicated that the medium and low P containing Ni coatings remained bright in appearance without pitting, showing good corrosion resistance. X-ray diffraction and SEM were used to study the as-plated specimens, showing that the P content has significant effect on the crystal structure and internal stress of coatings. The effects of the plating solution composition on the phosphorous content in the coatings, the deposition rate and corrosion property were also discussed.

11:45 AM
Corrosion Behavior of Pure Magnesium in Sodium Sulfate Solution: *Yar-Ming Wang*[1]; Surender Maddela[1]; [1]General Motors Research & Development Center

The corrosion behavior of pure magnesium in sodium sulfate solution wasstudied to establish a baseline understanding for magnesium alloy corrosion in different pH environments. Electrochemical techniques such as potentiodynamic polarization measurements, electrochemical impedance spectroscopy (EIS) and weight loss methods were compared. SEM examinations were conducted on the corroded surface and the cross-section to characterize the corrosion product and to observe the evolution of corrosion process. A six-element equivalent circuit model was used to describe active and passive corrosion behavior of magnesium in 1N sodium sulfate solution at different pH values. Due to the formation of a stable corrosion film, the corrosion current (icorr) at pH 13 was two orders of magnitude lower than at pH 8. Immersion corrosion tests showed that the weight loss at pH 8 increased linearly with time. However, for pH 12 and 13 solutions, the corrosion stopped once the passive film was formed. The importance of corrosion test duration is also described in this paper.

Magnesium Technology 2006: Primary Production, Recycling and Environmental Issues

Sponsored by: International Magnesium Association, TMS Light Metals Division, TMS: Magnesium Committee
Program Organizers: Alan A. Luo, General Motors Corporation; Neale R. Neelameggham, US Magnesium LLC; Randy S. Beals, DaimlerChrysler Corporation

Monday AM — Room: 6A
March 13, 2006 — Location: Henry B. Gonzalez Convention Ctr.

Session Chairs: Neale R. Neelameggham, US Magnesium LLC; Howard I. Kaplan, US Magnesium LLC

8:30 AM Introductory Comments Alan Luo, Symposium Chairman

8:40 AM
Simulation of Atmospheric Environments for Storage and Transport of Magnesium and Its Alloys: Guangling Song[1]; Sarath Hapugoda[1]; David St. John[1]; *Colleen Bettles*[1]; [1]CRC for Cast Metals Manufacturing

An environmental simulation system was developed to simulate the natural atmospheric environments that could be experienced by magnesium and its alloy ingots during their storage and transport. Magnesium, AZ91D and AM60 ingots were exposed to cycling temperature and humidity conditions in the environment simulation system and the surface degradation of the specimens was determined by measuring their brightness. It was found that the specimen surfaces exposed to the simulated atmospheric environments became duller and the degradation process was accelerated at a higher temperature or higher relative humidity. The presence of salt fog was quite detrimental to the specimen surfaces. AZ91 and AM60 with aluminium as a major alloying element were more resistant to the surface degradation than commercial purity magnesium. It is concluded that controlling humidity is a practical way of preventing rapid surface degradation of magnesium and its alloys during their storage and transport.

9:05 AM

Literature Review on Magnesium Recycling: Amjad Javaid[1]; *Elhachmi Essadiqi*[1]; Stacy Bell[2]; Boyd Davis[2]; [1]Material Technology Laboratories/ CANMET; [2]Kingston Process Metallurgy Inc.

Over the last decade, magnesium recycling has become more important because of the increasing use of the metal in transportation as a lightweight material for fuel economy. In order for magnesium to continue to grow, all forms of magnesium scrap need to be recycled - for both economic and environmental reasons. Today, only high-grade magnesium scrap is being recycled and more than half of the remaining low-grade magnesium scrap cannot be processed economically due to the inability of current sorting and refining technologies to adequately separate and clean the variety of scrap produced. The presence of impurities in magnesium can lead to embrittlement and poor corrosion resistance. Therefore, with the increased use of magnesium there is a growing need for more effective magnesium sorting and refining systems for recycling of all scrap types. This paper reviews current magnesium sorting and refining technologies and explores new techniques on the near horizon.

9:30 AM

Nb-Doped TiO_2 Inert Anodes for Electrolytic Production of Magnesium Metal: *Asem Mousa*[1]; Yong Yan[1]; Mark Pownceby[1]; Mark Cooksey[1]; Ken McDonald[1]; Marshal Lanyon[1]; [1]CSIRO

The synthesis and performance of polycrystalline niobium-doped titanium dioxide mixtures for use as potential inert anodes in magnesium electrowinning cells were investigated. The anode materials were prepared by solid-state reaction between niobium pentoxide and titanium dioxide. The effects of the Nb:Ti ratio, sintering temperature, oxygen partial pressure and the heating/cooling rates on the chemical (solid solution range) and physical (electrical conductivity, porosity, mechanical stability) properties of the anodes material determined. Subsequent testwork examined the electrochemical behaviour of the anodes in a molten mixed chloride bath operating at 700°C. The impact of key parameters including electrolysis time, current density and bath composition on the physical properties of the anodes were investigated.

9:55 AM Break

10:15 AM

The Physical Chemistry of the Carbothermic Route to Magnesium: *Geoffrey Alan Brooks*[1]; Michael Nagle[1]; Simon Trang[1]; [1]CSIRO Minerals

The carbothermic route to magnesium has significant potential to produce cheap magnesium but critical issues associated with the physical chemistry of various proposed processes and practical engineering dilemnas have prevented this route from being commercialized. This paper will examine the basic chemistry of carbothermic reduction of magnesia to produce magnesium. The thermodynamics of the reduction reaction, the kinetics of the reduction reaction, the kinetics of reversion, the kinetics of condensation and the distribution of impurities between phases will be critically reviewed and their potential impact on industrial processing discussed.

10:40 AM

Study on the Protecting Effect of HFC134 on AZ91D Magnesium Alloy in a Sealed Melting Furnace: Shu-Hong Nie[1]; *Shou-Mei Xiong*[1]; [1]Tsinghua University

The effects of holding time, temperature, furnace seal quality and stirring on the protection of AZ91D magnesium alloy were investigated in a sealed melting furnace under N2 atmosphere containing 0.01%vol. HFC134 filled once before the experiments. The morphology, thickness, and composition of the surface film were also studied. The results showed that the highest protecting temperature was 864°. At 790°, the effective protection time for AZ91D melt exceeded 10 hours, and the allowable pressure rising velocity in crucible exceeded 10000Pa/min. With surface stirring at a temperature lower than 800°, the new protective films were formed quickly. With the increase of the holding time and temperature, the carbon content in surface films decreased quickly to zero, and the oxygen content increased. The surface morphology of all protective films was a compacted cellular structure with an evenly distributed thickness of about 1~2 μm, whereas that of unprotective films was a wadding like structure.

11:05 AM

Thermal Decoating of Magnesium – A First Step towards Recycling of Coated Magnesium: *Christina Elizabeth Meskers*[1]; Anne Kvithyld[2]; Markus A. Reuter[1]; Thorvald Abel Engh[2]; [1]Delft University of Technology; [2]Norwegian University of Science & Technology

Die-cast magnesium is increasingly used for automotive applications and consumer electronics. For protective and decorative purposes it is coated. When the end-of-life goods are processed considerable amounts of coated magnesium scrap are generated. Currently this scrap is not recycled, leaving a resource unused. To close the magnesium utilization cycle the influence of coatings on the remelting process needs to be determined. As a first step thermal decoating of scrap prior to melting is investigated. Four objects were decoated in a thermobalance coupled to an online mass spectrometer. Decoating took place in argon and air using three heating rates. The mass loss, enthalpy and evolved gases were measured. The remaining residue was characterized. The results indicate the different stages in degradation. The combustion stage is only present using air, removing all organic matter. The residue is a mixture of pigments, fillers and conversion coatings. Decoating kinetics are assessed using iso-conversional models.

11:30 AM

Magnesia Solubility in the LaCl3-MgCl2 System: *Jian-Hong Yang*[1]; Timothy J. Scarpinato[1]; Donald G. Graczyk[1]; John N. Hryn[1]; [1]Argonne National Laboratory

Magnesia direct electrolysis is appealing to primary magnesium production because of significant cost savings that could result from simplified feed preparation. The key is to find a support electrolyte that has an acceptable solubility of magnesia. The LaCl3-MgCl2 system is one of the proposed electrolyte systems, but details of magnesia solubility measurements in this system have not been published. In this work, magnesia solubility in the LaCl3-MgCl2 system is presented.

Materials in Clean Power Systems: Applications, Corrosion, and Protection: Hydrogen Transport and Separation

Sponsored by: The Minerals, Metals and Materials Society, TMS Structural Materials Division, TMS/ASM: Corrosion and Environmental Effects Committee

Program Organizers: Zhenguo Gary Yang, Pacific Northwest National Laboratory; K. Scott Weil, Pacific Northwest National Laboratory; Michael P. Brady, Oak Ridge National Laboratory

Monday AM	Room: 212B
March 13, 2006	Location: Henry B. Gonzalez Convention Ctr.

Session Chairs: Petros Sofronis, University of Illinois at Urbana-Champaign; Truls Norby, University of Oslo

8:30 AM Introductory Comments

8:35 AM Keynote

State and Transport of Hydrogen in Oxides: *Truls Norby*[1]; [1]University of Oslo

The state and transport of hydrogen in oxides is important in several clean energy technologies; proton conducting electrolytes, mixed proton-electron conducting hydrogen seperation membranes, and recently for the functioning of oxides for novel electronics and photovoltaics. In addition to protons, the role of neutral hydrogen (atoms or molecules) is becoming clearer. The role of hydrogen in corrosion processes is well documented, but the detailed understanding suffers from the complexity of the process and the wide span in oxygen activity often encountered. The latter may cause all three oxidation states of hydrogen to take part. The talk attempts to look at hydrogen in oxides in the broad perspective of all the technological and scientific fields mentioned. One easily reaches the conclusion that we are in need of better characterisation and modelling of thermodynamics and transport of the three oxidation states of hydrogen in oxides.

9:20 AM Invited
Design of Inorganic Membranes for the Purification and Production of Hydrogen: *Brian Bischoff*[1]; [1]Oak Ridge National Laboratory

The U. S. is committed to a future hydrogen economy but hydrogen is not available as an elemental resource. There are many methods for producing hydrogen including coal gasification and using nuclear energy. Coal gasification offers one of the most versatile and cleanest ways to convert the energy content of coal into hydrogen. Hydrogen can also be produced using thermochemical cycles or high temperature electrolysis and the heat from a nuclear reactor. These processes can be improved by using inorganic membranes to perform separations at high temperatures in the presence of potentially corrosive gases. Inorganic membranes have the potential to remain stable under these conditions while performing the needed separations. Each of these applications has unique materials issues. The materials selection criteria and compatibility testing of membranes employed in these hydrogen related separations along with performance data will be presented.

9:50 AM
Co-Synthesis of Mixed-Conducting Composites for Hydrogen Membranes: *John S. Hardy*[1]; Nathan L. Canfield[1]; Jarrod V. Crum[1]; K. Scott Weil[1]; Larry R. Pederson[1]; [1]Pacific Northwest National Laboratory

Nanoscale powders comprising the two phases of mixed conducting composites for hydrogen membranes were co-synthesized through use of the glycine-nitrate combustion synthesis technique. Co-synthesis of proton conducting cation-doped barium cerate together with an electronic or oxygen ionic conducting phase results in an intimate mixture of the two phases with particle sizes on the order of 10 nm. The hydrogen permeability of membranes made from co-synthesized precursors will be discussed with emphasis on the effects of efforts to optimize composition, processing, and microstructure.

10:15 AM Break

10:30 AM Invited
Improving the Durability of Metal Membranes for Hydrogen Separation: *Stephen N. Paglieri*[1]; Dhanesh Chandra[2]; Iver E. Anderson[3]; Robert L. Terpstra[3]; Ronny C. Snow[1]; [1]Los Alamos National Laboratory; [2]University of Nevada, Reno; [3]Ames Laboratory

A durable, more cost-effective membrane material could be utilized extensively for purifying hydrogen in the chemical industries, and in the processes of generating, storing, and using hydrogen as an energy carrier. Two types of composite membranes were fabricated and tested: thin palladium and palladium alloy films supported on porous materials, and vanadium alloy foils coated with thin films (≤ 200 nm) of palladium and palladium alloys. Membrane strength and resistance to hydrogen embrittlement can be improved through the use of binary and ternary alloys of either vanadium or palladium. Another strategy for improving membrane performance, including mechanical durability and stability of hydrogen flux with time, includes supporting thin palladium alloy films on porous membranes that incorporate a diffusion barrier for metallic interdiffusion. The composite metal membranes were fabricated and characterized with respect to hydrogen permeability, permselectivity, and durability with respect to metallic interdiffusion, thermal cycling, and resistance to hydrogen embrittlement.

11:00 AM Invited
Processing of Ultrafine Alloy Powders for Hydrogen Membrane Substrates: *Iver E. Anderson*[1]; Robert L. Terpstra[1]; [1]Iowa State University

Controlled powder production by gas atomization can benefit emerging Fossil Energy technologies that utilize metal powders of sizes and types not produced efficiently by industry. Improved understanding and design of gas atomization nozzles has helped increase powder yields in special size classes, including ultra-fine (dia.<10 μm) and mid-range (10-75μm) powders, with reduced standard deviation. If adopted commercially, such improvements can lower a major technological barrier to new hydrogen membrane concepts or novel alloys for thermal spray coatings. To demonstrate process robustness, He atomization trials that produced ultra-fine Fe-16Al-2Cr (wt.%) powder were performed in an up-scaled system. Results of controlled sintering work to form porous sheets explored use of these ultra-fine spherical powders as substrates for hydrogen membranes. Narrow mid-range powder size distributions of elemental Cu and Al were nitrogen atomized using novel process parameters, anticipating trials on thermal spray alloys. Support from USDOE-FE (ARM) through Ames Laboratory contract No. W-7405-ENG-82.

11:30 AM Invited
Using First Principles Calculations to Screen Alloys for Hydrogen Purification Membranes: *David Sholl*[1]; Preeti Kamakoti[1]; Lymarie Semidey-Flecha[1]; [1]Carnegie Mellon University

Dense metal membranes can play a crucial role in the purification of H2 generated from coal gasification. A longstanding challenge has been to identify metal membranes that simultaneously give high membrane fluxes while being resistant to attack by common chemical contaminants in gasification streams. Alloys based on Pd have great potential as membranes with these properties, but experimental screening of multicomponent alloys as membranes is extremely resource intensive. We have developed a suite of methods based on rigorous coarse-graining of first principles quantum chemistry calculations that quantitatively predicts the flux of H2 through Pd-based alloy membranes (P. Kamakoti et al., Science 307 (2005) 569). The accuracy of these methods has been established by comparisons of theoretical predictions with extensive experimental data for Cu-Pd alloy membranes. We will describe how we are applying our methods to identify ternary alloys with promising performance as hydrogen purification membranes.

Materials Processing Fundamentals: Process Modeling

Sponsored by: The Minerals, Metals and Materials Society, TMS Extraction and Processing Division, TMS: Process Fundamentals Committee, TMS: Process Modeling Analysis and Control Committee
Program Organizers: Princewill N. Anyalebechi, Grand Valley State University; Adam C. Powell, Massachusetts Institute of Technology

Monday AM Room: 203A
March 13, 2006 Location: Henry B. Gonzalez Convention Ctr.

Session Chair: Adam Powell, Massachusetts Institute of Technology

8:30 AM
Fluid Flow and Transport Phenomena during Steel Refining and Casting Process: *Lifeng Zhang*[1]; [1]University of Illinois

The transport of fluid, heat ,and particles (bubbles and solid inclusions) in flowing molten steel is investigated in steel refining ladles, the continuous casting tundish, continuous casting mold and strand, and steel ingot casting processes. The two-equation k-e model is used to simulate the turbulence. Multiphase fluid flow is numerically simulated with a Lagrangian-Eulerian approach, an Eularian-Eulerian approach and the Volume Of Fluid (VOF) method. The simulation can predict inclusion trajectories, inclusion removal fraction, free surface waves and other phenomena, which can be used to optimize these important metallurgical operations.

8:55 AM
Numerical Simulations of Jet Break-Up Phenomena for the High Pressure Die Casting Process: *Valerio Viti*[1]; Kazunori Kuwana[1]; Adrian S. Sabau[2]; Mohamed Hassan[1]; Kozo Saito[1]; [1]University of Kentucky; [2]Oak Ridge National Laboratory

In the High Pressure Die Casting (HPDC) process, the molten metal is injected through a thin gate into the die cavity. High pressures and high gate velocities yield jet break-up and even atomization. In order to identify the effects that can negatively affect the final quality of the casting, jet break-up phenomena must be understood. In the present work, numerical simulations of the molten Mg flow through a high aspect-ratio rectangular gate are performed. Results are also presented for water analogue for an open. The numerical simulations used Volume of Fluid VOF-type (Eulerian) methods and Lagrangian methods. A sub-grid scale model was implemented that can be used in conjunction with VOF-type formulations to predict the break-up and atomization flow pattern. The proposed formulation was more efficient than traditional VOF methods since it does

not require the use of high-resolution grids. The numerical results were compared to experimental data for validation.

9:20 AM
Computational Simulation of Phase Change in Laser Cutting Process: *Sundar Marimuthu*[1]; Dipak Kumar Bandyopadyay[1]; Shankar Prasath Chaudhuri[1]; Pradir Kumar Dey[1]; [1]Jadavpur University

Laser cutting process is achieved by a combination of laser heating and the oxidation reaction of iron with oxygen. In this paper a three-dimensional simulation of phase change and heat transfer for a Laser Cutting process has been performed using a commercial computation fluid dynamics code, FLUENT. The melting process is incorporated using enthalpy-porosity technique and the phase change, is incorporated using Volume of Flow method. The governing equation is the transient three dimensional liquid fraction, momentum and energy equations for primary and secondary phase with appropriate boundary conditions. Transient temperature distribution, melting and phase change has been predicted. The developed model successfully estimated the kerf width at the inlet and exit and optimal speed required for defect free cutting. Three-dimensional simulation and visualization of the melting and phase change behavior inside the kerf was possible, thus enabling optimum processing windows to be predicted.

9:45 AM
Mathematical Modeling and Design of Heat Pipe-Cooled Metallurgical Furnace Equipment: *Pietro Navarra*[1]; Hujun Zhao[1]; Frank Mucciardi[1]; Tim Van Rompaey[2]; [1]McGill University; [2]Umicore Research

Cooling of critical furnace equipment to produce freeze lining is of particular interest as many metallurgical processes are intensified while attempting to prolong campaign life. This idea was combined with high-capacity heat pipes in the design of a copper slag launder. The design methodology of the launder and heat pipe cooling system is examined in this paper. With reliable material properties and operating conditions, CFD was used to quantitatively predict the skull thickness and the corresponding heat load applied to the slag launder. The operational limitations of heat pipe technology were considered and an appropriate cooling system was incorporated. Parametric modeling was used to simulate several launder and heat pipe configurations. The generated results were then used to optimize the design of the launder, which was built and tested in August of 2005. The experimental performance of the cooling system is evaluated and compared with the model results.

10:10 AM Break

10:25 AM
Computer Modeling Methodology of the Tecnored Ironmaking Process: José Carlos D'Abreu[1]; *Jose H. Noldin*[2]; Hélio Marques Kohler[3]; [1]Catholic University of Rio de Janeiro; [2]Tecnored/PUC-Rio; [3]Independent

The Tecnored process is a new ironmaking technology, developed on a unique approach that combined the interaction of empirical and theoretical knowledge, backed by extensive tests carried out in a dedicated pilot-plant and with close support of universities and research centers. Campaigns in the pilot-plant focused on understand, simulate and operate different reactor sizes, including a full size modular slice of the industrial furnace, which provided real-life conditions to develop the main features of the process such as internal dimensions, flame engineering, raceway pattern, thermal and gaseous profiles, formation, shape and maintenance of the melting zone, besides provide reliable data to feed and calibrate a special mathematical process modeling. This paper presents the methodology applied in this modeling, with special focus on the upper shaft of the furnace (zone of solid state reduction). The first results of this modeling are given and discussed in the end of the paper.

10:50 AM
Study of Non-Wetting Liquid Flow in a Bed of Monosized Particle Packing under the Influence of Lateral Gas Injection: *Vikrant Singh*[1]; Govind Saran Gupta[1]; [1]Indian Institute of Science

Gas-liquid(non-wetting) contacting in packed bed is a common operation in metallurgical reactors. Research has shown that, unlike wetting flow, non-wetting liquid flows in the form of discrete droplets or rivulets. Thus, modeling of liquid phase as a continuum is in contradiction to observations. Also, for the non-wetting case, continuum models have failed to describe liquid flow path when the liquid source is a point source. The aim of the current work is to put forward a combined lagrangian-eulerian approach to model liquid and gas flow in the packed bed. Liquid is assumed discrete and modeled using a force balance approach. Gas is assumed to be interpenetrating continua and modeled using k-epsilon model for turbulent flow. Structured packing is assumed and x-ray imaging technique used to visualize liquid flow lines in the bed. Simulation results for liquid flow path and liquid collection at bed bottom are compared with the experiments.

11:15 AM
Design of Supersonic Nozzles for Ultra-Rapid Quenching of Metallic Vapours: *Geoffrey Alan Brooks*[1]; Hasan Khan[1]; Peter Witt[1]; Tim Barton[1]; Michael Nagle[1]; [1]CSIRO Minerals

CSIRO has been experimenting with supersonic flows as a method of rapidly quenching metallic vapors. Cooling rates above one million degrees per second have been achieved. The supersonic flow conditions are achieved through adiabatic expansion of the gas through a Laval nozzle into a vacuum chamber. This paper will describe the basic physics of the process, outlining the CFD modeling of flow in the nozzle, the effects of different flow conditions on the condensation process and discuss the practical design issues associated with operating supersonic nozzles.

Multicomponent-Multiphase Diffusion Symposium in Honor of Mysore A. Dayananda: Phenomenology

Sponsored by: The Minerals, Metals and Materials Society, ASM Materials Science Critical Technology Sector, ASM-MSCTS: Atomic Transport Committee
Program Organizers: Yong-Ho Sohn, University of Central Florida; Carelyn E. Campbell, National Institute of Standards and Technology; Richard Dean Sisson, Worcester Polytechnic Institute; John E. Morrall, Ohio State University

Monday AM
March 13, 2006
Room: 203B
Location: Henry B. Gonzalez Convention Ctr.

Session Chairs: Alexander H. King, Purdue University; Richard Dean Sisson, Worcester Polytechnic Institute

8:30 AM Introductory Comments: Prof. Dayananda as a Collegue and Advisor

8:50 AM Invited
An Examination of Selected Multicomponent Diffusion Couples: *Mysore A. Dayananda*[1]; [1]Purdue University

Selected diffusion couples investigated in Cu-based and Fe-based multicomponent systems are examined for zero-flux plane development, interdiffusion up activity gradients, and unusual diffusion paths. The couples are analyzed for interdiffusion fluxes and interdiffusion coefficients with the aid of "MultiDiFlux©" program. The variations of interdiffusion coefficients over various composition ranges within the diffusion zone are assessed in terms of eigenvalues and eigenvectors determined from interdiffusion coefficient matrices. The internal constraints on the diffusion paths are explored in terms of fluxes of the individual components and their variation with composition. These constraints are discussed with application to selected couples. The research is supported by the National Science Foundation.

9:20 AM
A Transfer Matrix Approach for Analysis of Multicomponent Diffusion Couples: *L. R. Ram-Mohan*[1]; Mysore A. Dayananda[2]; [1]Worcester Polytechnic Institute; [2]Purdue University

A transfer matrix approach is presented for the development of solutions to diffusion problems in multicomponent systems. Expressions are derived for a transfer matrix and its integral so that the fluxes of the individual components can be obtained at any coordinate x, given an initial value for the fluxes or the concentration gradients at an initial position x_s. Interdiffusion coefficients are determined as average values over various

regions selected in the diffusion zone by the method of moments developed by Dayananda and Sohn. Expressions for concentrations are also obtained from initial conditions on fluxes or concentration gradients. The method employing the matrix approach is applicable to any number of components and may be considered as a generalization of the solutions of Fujita and Gosting originally developed for ternary diffusion. The method is illustrated with an application to a multicomponent diffusion couple.

9:45 AM
Effect of Diffusivity Variations on Interdiffusion Microstructures: *John E. Morrall*[1]; Yunzhi Wang[1]; [1]Ohio State University

The mathematical equations that describe diffusion couples are greatly simplified by assuming that the diffusivity is constant. To quote a famous modeler "with (constant) diffusion everything is error functions." The error function predictions are simplified too, for they predict concentration profiles, diffusion paths, and zero-flux planes that are symmetric with respect to the initial diffusion couple interface and they predict well defined rules for interdiffusion that can be generalized for n-component systems. However both the symmetry and the rules are broken when the diffusivity varies with composition. Professor Dayananda has made important contributions to the field of diffusion by documenting what happens when the diffusivity varies through his experimental work on multicomponent, multiphase systems. These contributions will be outlined along with other known consequences of diffusivity variations.

10:10 AM Break

10:30 AM Invited
Some Aspects of Interface Migration in Ternary Systems: *Gary R. Purdy*[1]; [1]McMaster University

In recognition of Professor Dayananda's many contributions to our knowledge of multicomponent-multiphase effects, this contribution will focus on certain aspects of transformation interface migration that can be ascribed specifically to the presence of a third element. Some examples considered include (a) liquid film migration in ternary alloy systems, and (b) the role of substitutional alloying elements in the coarsening of carbides in steels and in the growth of ferrite from austenite.

11:00 AM Invited
Aspects of Diffusional Reactions in Multi-Component, Multi-Phase Systems: *John Agren*[1]; [1]Royal Institute of Technology

Most practical applications of diffusion theory, within heat treatment and degradation of materials, are not only multicomponent but do also involve several phases that may form or dissolve as a consequence of diffusion. Phase-field modeling is superior in some aspects and allows a detailed prediction of the evolution of one or a few particles. Nevertheless, it has a number of shortcomings that makes it less applicable to solve many practical problems. Some of these shortcomings may be overcome by "effective" models like the ones developed by Hopfe and Morral and by Engström and Ågren. The latter models have turned out to be surprisingly useful to solve a number of practical problems. In this presentation the methods will be summarized and some applications will be reviewed. Some problems of fundamental character will be discussed and some recent advances will be presented.

11:30 AM Invited
Outside the Box of Phenomenological Diffusion Formalism: *Robert T. DeHoff*[1]; [1]University of Florida

Professor Dayananda and I have shared an interest in mutlicomponent and multiphase diffusion for more than three decades. We have enjoyed many periodic palavers at meetings such as this one through the years. He always has something new and interesting on the front burner. We have learned each other's prejudices on the subject and respect them. He knows that one of my pet prejudices is a dissatisfaction with the traditional phenomenological formalism which is used almost exclusively to describe diffusion behavior in these complex systems, and a desire to devise descriptions in terms of parameters that actually have understandable physical meaning. This presentation reviews a litany of problems associated with the ubiquitous phenomenological theory. None of these complaints is new; they are widely known and widely ignored. It may be argued that the importance and significance of these problems lies perhaps in the eye of the beholder. There is half a century of theoretical inertia that discourages thinking outside the phenomenological box. Also reviewed is a description of diffusion behavior that is outside this box. This jump frequency formalism is couched in terms of parameters with physical meaning, but brings some problems of its own.

12:00 PM Invited
Discontinuities in Kirkendall Velocity in Multiphase Diffusion Couples: *William J. Boettinger*[1]; Jonathan E. Guyer[1]; Carelyn E. Campbell[1]; [1]National Institute of Standards and Technology

In multiphase binary diffusion couples that maintain planar interfaces between phases, experimental evidence and analysis by van Loo et al. have revealed interfacial discontinuities in the Kirkendall velocity. Under the usual assumptions of the diffusion model for the Kirkendall effect, the magnitude of the discontinuity is proportional to the difference of the differences of the intrinsic diffusion coefficients for each phase. Questions arise about the implications of the discontinuity in the context of the deformation and stress state in the diffusion couple. To clarify these points, we examine the moving interface problem using the Cahn-Hilliard equation applied to a solid solution with a miscibility gap. The predicted Kirkendall velocity is continuous but suffers a large change across the diffuse interface. The associated displacement fields and strains are also continuous.

Point Defects in Materials: New Techniques

Sponsored by: The Minerals, Metals and Materials Society, TMS Electronic, Magnetic, and Photonic Materials Division, TMS Structural Materials Division, TMS: Chemistry and Physics of Materials Committee
Program Organizers: Dallas R. Trinkle, U.S. Air Force; Yuri Mishin, George Mason University; David N. Seidman, Northwestern University; David J. Srolovitz, Princeton University

Monday AM — Room: 210B
March 13, 2006 — Location: Henry B. Gonzalez Convention Ctr.

Session Chair: Dallas R. Trinkle, U.S. Air Force

8:30 AM Invited
Atom-Scale Studies of Solids Using Hyperfine Interactions: *Gary S. Collins*[1]; [1]Washington State University

We have investigated intermetallic compounds over 15 years through measurements of nuclear quadrupole interactions using the method of perturbed angular correlation of gamma rays, with radioactive probe atoms introduced at the ppb level. Three applications will be discussed: (1) Point defects arising due to deviations from stoichiometry and/or thermal activation can be distinguished by characteristic interactions; (2) Sublattices occupied by impurity probes can be identified from the magnitude and symmetry of measured electric field gradients; (3) Jump frequencies of diffusing probe atoms can be determined through relaxation of the nuclear quadrupole interaction. Such studies not only provide insight into atomistic phenomena such as defect agglomeration or switching of solute atoms between sublattices as a function of composition or temperature, but will be shown to yield measurables such as defect concentrations, activation enthalpies for defect formation and migration and for solute transfer between sublattices, and probe-atom jump frequencies.

9:00 AM Invited
Quantum Monte-Carlo Examines Accuracy of Density Functionals for Interstitial Defects in Silicon: *Richard G. Hennig*[1]; Kevin Driver[1]; William Parker[1]; Cyrus J. Umrigar[2]; John W. Wilkins[1]; [1]Ohio State University; [2]Cornell University

Silicon displays a variety of interstitial defects. Ion-implanted silicon interstitials nucleate extended {311} planar defects limiting device fabrication and performance. Quantum Monte-Carlo calculations for interstitial silicon defects determine accurate defect formation energies that test the accuracy of current density-functionals. Stable defect structures from accelerated tight-binding molecular dynamics are relaxed with density-functional methods to confirm their stability. More than a dozen new stable interstitial clusters are discovered[1]. While density-functional determined

structures are reliable, defect energies are sensitive to the exchange-correlation functional. Quantum Monte Carlo correctly predicts the experimental cohesive energy, lattice constant, and bulk modulus of silicon. For interstitial defects in silicon, quantum Monte Carlo shows that local-density and gradient-corrected functionals underestimate the defect energies by about 1 eV. [1]D.A. Richie et al. Physical Review Letters 92, 45501 (2004).

9:30 AM Invited

Defects and Off-Stoichiometry in Alloys and Oxides from First-Principles: *Anton Van der Ven*[1]; [1]University of Michigan

First-principles computational schemes have reached a stage where they can be used to predict a wide range of materials properties with reasonable accuracy. Most materials are multi-component and contain dilute concentrations of impurities or defects such as vacancies. Predicting thermodynamic and kinetic properties of these materials from first-principles requires an accurate description of their configurational degrees of freedom as configurational entropy plays an important role at finite temperature. The cluster expansion has proven to be a powerful tool to extrapolate first-principles energies to the energy of any state of disorder within a multicomponent solid. In this talk, I will describe the latest developments in first-principles alloy theory and show how it can be used to predict the thermodynamic properties of vacancies within alloys and oxides.

10:00 AM

Thermochemistry of Point Defects in PuO(2-X): Petrica Cristea[1]; *Marius Stan*[1]; [1]Los Alamos National Laboratory

We developed a thermochemical model to predict the behavior of hypostoichiometric plutonia under different temperatures and partial pressures of oxygen. Based on the observed similarities between CeO(2-x) and PuO(2-x), five types of point defects were considered as major contributors to the thermochemical properties of PuO(2-x): the reduced plutonium ions Pu(3+), two types of oxygen vacancies, and two types of Pu(3+)-oxygen vacancy clusters. A number of example applications, such as the calculation of partial Gibbs free energy of oxygen, nonstoichiometry, defect configuration entropy, and the behavior of chemical potential of defect species at different oxygen deficiencies are presented in order to highlight some of the current capabilities of the approach. Advanced topics such as calculation of self and chemical oxygen diffusivities as a function of nonstoichiometry and temperature are addressed. The results are validated against available experimental data on nonstoichiometry and oxygen diffusivity.

10:20 AM Break

10:35 AM Invited

High Resolution Materials Studies with the Magnetic Resonance Force Microscope: *P. Chris Hammel*[1]; Tim Mewes[1]; Jongjoo Kim[1]; Sharat Batra[2]; Denis Pelekhov[1]; Palash Banerjee[1]; Kin Chung Fong[1]; Yuri Oboukhov[1]; [1]Ohio State University; [2]Seagate Technology

The magnetic resonance force microscope (MRFM) is a novel scanned probe instrument which combines the three-dimensional imaging capabilities of magnetic resonance imaging with the high sensitivity and resolution of atomic force microscopy. It will enable non-destructive, chemical-specific, high-resolution microscopic studies and imaging of subsurface properties of a broad range of materials. Here we present the principles of the MRFM and discuss applications of the MRFM to the detection of NMR, ESR and Ferromagnetic Resonance (FMR). As an example we present studies of investigations of the dynamic magnetic properties of permalloy disc arrays using ultrasensitive low temperature ferromagnetic resonance force microscopy. Local spectroscopy reveals properties of the dot array and local information about individual dots. The ferromagnetic resonance of a dot in the presence of the tip field enables us to clearly resolve individual 50 nm thick dots with a 1.5 micron diameter.

11:05 AM

Compositional Point Defect Evaluation Using Diffusion Experiments: *Ji-Cheng Zhao*[1]; Xuan Zheng[2]; David G. Cahill[2]; [1]General Electric Company; [2]University of Illinois at Urbana-Champaign

Compositional point defects such as vacancies and anti-sites have a significant effect on the properties of alloys and intermetallic compounds. For instance, the formation of point defects in NiAl results in three orders of magnitude change in its diffusion coefficients. There are two indirect ways to find the formation of compositional point defects in alloys and intermetallics using diffusion couples/multiples. The first one is to use a novel micro-scale thermal conductivity probe to measure thermal conductivity across a concentration gradient. A sharp change in thermal conductivity in a very narrow range of composition is indicative of compositional point defect formation. Thermal conductivity measurements can also be used to study the site preference/elemental substitution in intermetallic compounds. The second method is to examine the shape of diffusion profiles. Examples will be used to illustrate these methodologies. Both methods are sufficient, but not necessary tests of the compositional point defects.

11:25 AM Invited

Structure and Mobility of Defects Formed in Collision Cascades in Ceramics: *Blas Pedro Uberuaga*[1]; [1]Los Alamos National Laboratory

The evolution of radiation damage is a problem spanning many time and length scales. Damage production occurs on the atomic scale via collision cascades that last picoseconds. This damage manifests itself macroscopically as swelling or cracking which can take years to develop. There is a wide range of phenomena inbetween, including defect diffusion, the formation of loops and voids, and the development of more complex microstructure. We apply several simulation techniques to study damage production and evolution in ceramic materials. Using molecular dynamics, we study low-energy cascades in MgO and MgAl2O4. We use temperature accelerated dynamics to probe the long-time evolution of the resulting damage. A surprising picture emerges for MgO, with large interstitial clusters being very mobile. Using these results, we have developed a rate theory model describing the formation of dislocation loops in MgO, where we see an impact of the mobile clusters on loop size.

11:55 AM

Kinetic Monte Carlo Studies of Radiation Induced Segregation in Metal Alloys: Joerg Rottler[1]; *David J. Srolovitz*[1]; Roberto Car[1]; [1]Princeton University

In irradiated metals, the material degradation is largely controlled by point defects that are produced in collisions between the energetic particles and the host atoms. In alloys, point defect fluxes to sinks such as grain boundaries and free surfaces may cause radiation induced segregation. The alloy composition is dynamically changed due to point defect concentration gradients and different couplings between the host atoms and defects. We perform a detailed comparison between kinetic Monte Carlo simulations and the continuum rate-diffusion theory of RIS. In the absence of thermodynamic effects, continuum theory agrees well with kMC provided that correlation effects are accurately taken into account. Standard treatments of alloy thermodynamics on the level of regular solution theory are shown to be inconsistent with the kMC results. We suggest corrections to the continuum theory that provide good agreement with the numerics and also consider specifically thecase of FeCr.

Separation Technology for Aqueous Processing: Session I

Sponsored by: The Minerals, Metals and Materials Society, TMS Extraction and Processing Division, TMS: Aqueous Processing Committee, TMS: Copper and Nickel and Cobalt Committee, TMS: Lead and Zinc Committee, TMS: Process Fundamentals Committee
Program Organizer: Robert L. Stephens, Teck Cominco Metals Ltd

Monday AM — Room: 202B
March 13, 2006 — Location: Henry B. Gonzalez Convention Ctr.

Session Chair: Courtney A. Young, Montana Tech of the University of Montana

8:30 AM

Bioleaching of Nickel Laterite Ores Using Halotolerant Aspergillus Foetidus under Saline Conditions: *Anat Deepatana*[1]; V. Thangavelu[1]; Jessica Annalishia Tang[1]; Marjorie Valix[1]; [1]University of Sydney

Biological leaching of low-grade nickel laterite is based on a non-traditional leaching of oxide minerals using heterotrophic micro-organisms.

The organisms solubilise metals by excreting organic acids; these acids then form complexes with heavy metals. High salinity of water supplies and soils in the vicinity of nickel laterite ore bodies is a major abiotic stress to fungi and represents a major challenge in the application of bioleaching process in-situ. Salinity exposes fungi cells to Na+ toxicity and osmotic stress. This study examined the salt tolerance development of Aspergillus foetidus based on gradual acclimatization of organism, its salt threshold and the salinity effect on its metabolism. The biological leaching of limonite and nontronite minerals with the resulting halotolerant organism under saline conditions was assessed. It was observed that salinity stress affected the organism's growth and energy utilization efficiency. Metal dissolution kinetics and capacity were equivalently influenced by salt stress.

8:55 AM

Ion Exchange Recovery of Nickel and Cobalt from Metal-Organic Complexes Generated in Bioleaching of Low Grade Nickel Laterite Ores: *Anat Deepatana*[1]; Marjorie Valix[1]; [1]University of Sydney

Bioleaching of nickel laterite ores is based on the use of heterotrophic fungi organisms and their metabolites (organic acids) to dissolve nickel and cobalt from oxide minerals to form metal-organic complexes. Metal recovery from this process using an aminophosphonic acid based chelating resin (Purolite S950) was investigated as a function of metal concentrations, complexing agent including citric, dL-malic and lactic acids. Batch adsorptions were conducted using synthetic leachate solutions of nickel and cobalt with concentrations from 15 to 2000 mg/L prepared in 0.01 and 0.1 M organic acids. Equilibrium adsorption data were fitted into the Langmuir and Freundlich models. Metal elution was conducted using 2 M nitric acid in which up to 90% of the metals where recovered. It was observed that the maximum adsorption capacities of nickel and cobalt were 3.26 and 10.48 mg/g resins respectively achieved in 0.01 M lactic acid.

9:20 AM

Kinetics of Limonite and Nontronite Ore Leaching by Fungi Metabolic Acids: *Anat Deepatana*[1]; Jessica Annalishia Tang[1]; Marjorie Valix[1]; [1]University of Sydney

Bioleaching of nickel laterite ores is the extraction technology based on the use of heterotrophic micro-organisms and their organic acid products to dissolve metals from oxide minerals. This study examined the chemical leaching kinetics of limonite and nontronite ores with pure fungi metabolites including citric, lactic and malic acids. Leaching was undertaken at 30°C, with ore pulp density of 2-10 g/L in acid concentrations 0.2- 3M for a period of 24 days. The chemical leaching data were compared to metal dissolution achieved with bioacids generated by Aspergillus foetidus grown in sucrose based substrate. Leaching was investigated as a function of acid type, acid activity, oxygen reduction potential, particle size and pulp density. The application of an ex-situ bioleaching process in extracting nickel and cobalt from laterite ores was assessed.

9:45 AM

Modeling of Electrodiffusion in Aqueous Processing: Witold Kucza[1]; *Marek Danielewski*[1]; Andrzej Lewenstam[1]; [1]AGH University of Science and Technology

The model of electrodiffusion (the ionic flow in various continuous media) based on the Nernst-Planck-Poisson equations (NPP) is presented. The NPP equations and the continuity equation, including the reactive term, are discretized in space and time. The resulting set of equations is solved numerically using the Rosenbrock method in Mathcad 12. The NPP model is used for simulations of transient and steady state concentrations and electric potential profiles. The impedance spectra of electrochemical systems with different boundary conditions are presented, including a permselective case. The method allows for obtaining the direct relationship between transport properties of the bulk solution and the interfaces (ionic diffusivities and heterogeneous rate constants) and the complex impedances of electrochemical systems. The method is applied for modeling of selective precipitation and ion exchange processes.

10:10 AM Break

10:25 AM

Semi-Batch Precipitation of Manganese from an Industrial Zinc Leach Solution Using SO2/O2: *Vincent Menard*[1]; George P. Demopoulos[1]; [1]McGill University

The purpose of the present work was to remove selectively manganese from a neutral leach zinc-rich solution ([Zn] =150 g/L) at 80°C using a gas mixture of sulphur dioxide (SO2) and oxygen (O2) as oxidizing agent. In order to determine the optimum conditions for manganese removal, several semi-batch experiments were performed, where the effects of pH, ORP, SO2/O2 ratio, mixing intensity, etc. were investigated. Results of these tests showed that SO2/O2 was a fast and effective oxidant for removing manganese down to ppm level provided that the appropriate reactor design, agitation and SO2/O2 ratio were employed.

10:50 AM

Study of Organic Phase Composition and Solvent Extractive Process for Purifying Nickel Chloride Solution with N235: *Chen Song*[1]; Wang Lijun[1]; Zhang Li[1]; Luo Yuanhui[1]; [1]General Research Institute for Non-Ferrous Metals

In the experiments of purifying the solution of chlorine leaching from nickel concentrate with N235, the effects of organic phase composition on purifying efficiency have been studied. From the results obtained, the optimal organic phase composition is found to be 25%+12%isomerous alcohol +63%sulfonic kerosene (V/V) and the saturated content of cobalt in organic phase is7.95 g·L-1. And then the serial experiment is carried out. The results show that at the given organic phase composition, the purified solution contains ρ(Ni) >200 g·L-1, ρ(Ni)/ ρ(Co) >50000 and the contents of Cu, Fe, Mn, Zn meet the technical criterion of standard nickel electrolyte. The cobalt chloride solution contains ρ(Co) >110 g·L-1, ρ(Co)/ρ(Ni)>50000 and the enrichment of cobalt has been achieved.

Solidification Modelling and Microstructure Formation: A Symposium in Honor of Prof. John Hunt: Dendritic Growth I

Sponsored by: The Minerals, Metals and Materials Society, TMS Materials Processing and Manufacturing Division, TMS: Solidification Committee

Program Organizers: D. Graham McCartney, University of Nottingham; Peter D. Lee, Imperial College; Qingyou Han, Oak Ridge National Laboratory

Monday AM — Room: 6C
March 13, 2006 — Location: Henry B. Gonzalez Convention Ctr.

Session Chairs: Graham McCartney, University of Nottingham; Martin Glicksman, Rensselaer Polytechnic Institute

8:30 AM Introductory Comments

8:35 AM Invited

Growth and Stability of Solidification Microstructures: *Rohit Trivedi*[1]; [1]Iowa State University

The key aspects of the theoretical models on cellular, dendritic and eutectic growth will be summarized with specific emphasis on the contributions made by John Hunt. These models will be validated through critical experimental studies in metallic and transparent systems. Emphasis will then be placed on the stability of these microstructures in bulk samples, and it will be shown that the stability conditions in 3D growth are significantly different from those in the 2D systems. The differences in these stability conditions will be discussed and the role of the additional degree of freedom in the third dimension will be emphasized.

9:10 AM

Phase-Field Simulations of Rapid Solidification in Binary Alloys: Jun Fan[1]; Mikko Haataja[2]; *Nikolas Provatas*[1]; [1]McMaster University; [2]Princeton University

The kinetics of rapid solidification is important for alloys developed by powder metallurgy. The resulting powder microstructure and phase

composition controls the properties of the final solidification product. In this work, we carry out a quantitative study of rapid solidification kinetics in binary alloys using a phase-field model simulated with a novel adaptive mesh refinement algorithm in two spatial dimensions. At a high undercooling, we observe a morphological transition from dendritic to non-dendritic structures. Furthermore, growth velocity is shown to undergo a sharp transition at an undercooling that coincides with the transition in dendritic morphology. These results are shown to be in good agreement with experimental measurements. We elucidate the underlying mechanisms of these transitions and demonstrate that they are linked to non-equilibrium solute partitioning as the solute diffusion length becomes comparable to the interface width.

9:35 AM

3-D Numerical Simulation of Dendritic Crystal Growth with Phase-Field Model: *Tao Jing*[1]; Hongzhao Zhao[1]; Baicheng Liu[1]; [1]Tsinghua University

Three-dimensional simulation of the dendritic growth for aluminum alloy was studied by coupling with thermal noise. Macro-micro coupled method and a capturing liquid method were adopted here. Since 3-D numerical simulation takes too much calculation, thermal noise was only added at the cell interface instead of the whole cell. When the dendrite grows, the capturing liquid method captures the liquid cells into the interface ones and pushes the interface region forward. Three-dimensional simulation of multiple grains for aluminum alloy was also realized. Different optimized growing directions were introduced in multi-grains simulation, which makes the simulation more coincident with the practical case. One parameter of dendritic growth interface was introduced to distinguish the original grains with different optimized growing directions. The simulation result was compared with those obtained experimentally.

10:00 AM Break

10:15 AM Invited

Dendrite Growth Directions in Al-Zn Alloys: Frédéric Gonzales[1]; *Michel Rappaz*[1]; [1]Ecole Polytechnique Fédérale de Lausanne

Recent investigations on aluminum-base alloys have revealed that dendrites can grow along various directions as a result of the low anisotropy of the interfacial energy (less than 1%). In this area, Al-Zn alloys provide a unique system, as the hcp (and much more anisotropic) Zn element can be diluted up to 95wt% in the liquid phase while still producing fcc dendrites during solidification. In specimens which have been directionally solidified or grown in a Bridgman furnace, a gradual transition from <100>- to <110>-dendrites has been observed when the zinc concentration is gradually increased: <100> dendrites form up to about 30wt% of Zn, while <110> dendrites are clearly observed above 75wt%. Such measurements should allow a correlation between the anisotropy of the interfacial energy and the zinc concentration to be made, thus providing useful information for molecular dynamic simulations of the solid-liquid interfacial energy/stiffness.

10:40 AM

Diffuse and Sharp Interface Approaches to Thermosolutal Dendritic Growth: *Juan C. Ramirez*[1]; Pinghua Zhao[2]; Juan C. Heinrich[2]; [1]Los Alamos National Laboratory; [2]University of New Mexico

We model the equiaxed dendritic solidification of dilute binary alloys into an undercooled melt with a finite element based interface tracking technique (sharp interface approach) as well as a phase-field technique (diffuse interface approach). This type of problem exhibits a complex interplay of species and heat diffusion combined with interface movement. Although equiaxed dendritic growth appears to be well understood in many respects, its direct numerical simulation still represents a major challenge, even in two dimensions. For different values of undercooling, grain orientation and initial melt concentration, we use both diffuse and sharp interface approaches and discuss the features associated with each approach while comparing the results obtained. We observe that relatively minor changes in physical conditions can affect significantly the difficulty of obtaining a solution to the problem, regardless of the approach employed. The organic system succinonitrile-acetone, popular with experimental researchers, is used as the substance in all simulations.

11:05 AM

Study of the Dendritic Growth in Directional Solidification of Bulk Transparent Alloys: *Cédric Weiss*[1]; Nathalie Bergeon[1]; Nathalie Mangelinck-Noel[1]; Bernard Billia[1]; [1]L2MP

A directional solidification facility, developed by CNES (French Space Agency) in the frame of the DECLIC project, enables the in situ and real time characterization of the solid-liquid interface on bulk transparent materials. The optical diagnostics of this device provide top and side views of the interface during the solidification of the alloy (succinonitrile based) contained in a long cylindrical glass crucible. Results of columnar dendritic growth studies performed with the laboratory model of this solidification furnace, especially focusing on pattern formation and characterization will be presented here. To extend the range of solidification parameters available and of corresponding microstructure types, a power-down furnace has also been developed in the laboratory for bulk transparent alloys. The very low thermal gradients obtained with this furnace have enabled the very first observations of superdendritic growth and columnar-to-equiaxed transition in this kind of systems.

11:30 AM

A 6-Site Force Field for Succinonitrile and Its Crystal-Melt Interfacial Free Energy Anisotropy: *Xiaobing Feng*[1]; Brian B. Laird[1]; [1]University of Kansas

A 6-site succinonitrile force field has been developed. The model has produced proper proportions of the succinonitrile conformers, which is necessary to avoid the thermal contraction of the plastic crystal phase around melting point. The initial charges are obtained with quantum chemistry calculations, and they are adjusted to improve the melting point while keeping the dipole moment fixed at 5.7 Debye. The melting point of the model has been adjusted using the Gibbs-Duhem integration method. The melting point of the model, determined by using interface method, is in good agreement with experiment. Using the fluctuation spectrum method and the new force field we calculated the crystal-melt interfacial free energies. The preliminary results are: the average free energy is 7.15×10^{-3} (Jm^{-2}), and the anisotropy parameter (ε_4) is ~0.2%. (For a two-dimensional case, the free energy is expressed as $\gamma(\theta)=\gamma_0[1+\varepsilon_4\cos(\theta)]$). The amplitude of the free energy is in agreement with experiment.

11:55 AM Invited

Non-Equilibrium Segregation in Alloys: *Kenneth A. Jackson*[1]; [1]University of Arizona

During growth the segregation coefficient increases from the equilibrium value as the growth rate increases. This effect has been well documented experimentally for small concentrations of dopant in rapidly crystallized silicon, and has been studied in detail using Monte Carlo computer simulations. These simulations also predict that the non-equilibrium distribution coefficient is strongly dependent on composition for non-dilute alloys. There is a change in the growth direction of ammonium chloride dendrites from <100> to <111> in ammonium chloride-water solutions. It is suggested that this change in growth direction is due to increased anisotropy in the distribution coefficient with increasing growth rate. A significant increase in distribution coefficient is predicted to be a general phenomenon which occurs at nominal growth rates in non-dilute alloys.

Space Reactor Fuels and Materials: Refractory Alloy Properties and Welding

Sponsored by: The Minerals, Metals and Materials Society, ASM International, TMS Structural Materials Division, TMS/ASM: Nuclear Materials Committee, TMS: Refractory Metals Committee
Program Organizers: David James Senor, Pacific Northwest National Laboratory; Brian D. Wirth, University of California; Robert Hanrahan, Los Alamos National Laboratory; Steven J. Zinkle, Oak Ridge National Laboratory; Mehmet Uz, Lafayette College; Evan K. Ohriner, Oak Ridge National Laboratory; Brian V. Cockeram, Bechtel Bettis Inc

Monday AM Room: 213B
March 13, 2006 Location: Henry B. Gonzalez Convention Ctr.

Session Chairs: David James Senor, Pacific Northwest National Laboratory; Brian V. Cockeram, Bechtel Bettis Inc

8:30 AM
Processing, Microstructure and Properties of Nb – Zr – C Alloys. I. Microstructure Characterization of Tube and Sheet Products: *Mehmet Uz*[1]; Robert H. Titran[2]; [1]Lafayette College; [2]NASA Glenn Research Center

We studied the effects of processing and high temperature exposure on microstructures of Nb-1Zr–0.1C tubes and sheets. Tube shells were extruded 8:1 from a vacuum arc-melted ingot at 1900K and 1550 K. Tubes were fabricated from tube shells by cold drawing with in-process anneals. Sheets were fabricated by cold rolling bars that were single-, double- or triple-extruded 4:1 at 1900K. Both tube and sheet samples were double annealed (1h \@1755K+2h\@1475K) following fabrication. Some sheet samples were also exposed to 1350K and 1450K for up to 34,500h with/without applied load. Microstructure characterization included grain size measurement, chemical analysis, optical and electron microscopy, and analysis of phase-extracted residue of the samples. The results are presented with the emphasis on the effects of processing on the microstructure, and its high temperature stability.This work was performed for USDOE, Nuclear Energy, Reactor Sys. Development and Tech., Washington, D.C. 20545, under Interagency Agreement DE-Al03-86SF16310.

8:55 AM
Processing, Microstructure and Properties of Nb – Zr – C Alloys. II. Tensile, Creep and Microhardness Properties of Sheet Products: *Mehmet Uz*[1]; Robert H. Titran[2]; [1]Lafayette College; [2]NASA Glenn Research Center

This paper deals with the effects of thermomechanical processing on microhardness, tensile and creep properties of Nb-1wt.%Zr- 0.1wt.%C sheet. Sheet bars were cold rolled into 1-mm thick sheets following single, double, or triple extrusion operations at 1900K. All specimens were given a two-step heat treatment of 1h at 1755K+2h at 1475K prior to testing. Creep tests were conducted at 1350K and 34.5MPa for up to 34,500h, and at 1450K and 24MPa for up to 12,000h. Tensile properties were determined at both 300K and 1350K. Microhardness measurements were performed on samples at various stages of processing and testing. The results are discussed in correlation with thermomechanical processing and microstructure, and compared to results obtained from testing of Nb - 1 wt.%Zr and Nb - 1 wt.%Zr and 0.06 wt.%C alloys. This work was performed for USDOE, Nuclear Energy, Reactor Sys. Development and Tech., Washington, D.C. 20545, under Interagency Agreement DE-Al03-86SF16310.

9:20 AM
Factors Affecting the Texture and Recrystallization of Annealed Nb-1Zr: *David T. Hoelzer*[1]; Scott A. Speakman[1]; Edward A. Kenik[1]; Steven J. Zinkle[1]; [1]Oak Ridge National Laboratory

The purpose of this study was to determine important factors influencing the thermal creep behavior of Nb-1Zr. In this study, a detailed experimentally-based study utilizing advanced characterization techniques including XRD pole mapping, EBSP mapping, and TEM was conducted in order to gain a better understanding of factors that may affect the texture and recrystallization of annealed Nb-1Zr. These factors included the magnitude and directionality of cold-deformation, annealing temperature, and heating rate. It was found that significant changes in texture occurred in Nb-1Zr depending on the deformation level, rolling direction as well as the time and temperature of annealing. The EBSP maps of annealed Nb-1Zr showed that the grains were distributed in groups that shared common texture components and low misorientation boundaries. Details of the texture results of Nb-1Zr will be presented and compared to those obtained from studies of the similar group VB metals V, Nb, and Ta.

9:45 AM
Effect of Texture on Creep Properties of Nb-1%Zr Alloy: *Yan Cui*[1]; Tim McGreevy[2]; David Hoelzer[2]; Steve Zinkle[2]; T. G. Nieh[1]; [1]University of Tennessee; [2]Oak Ridge National Laboratory

The creep properties of Nb-1%Zr alloy was evaluated with special emphasis on the texture effect. Fully crystallized Nb-1%Zr samples with various grain sizes and crystallographic textures were prepared from cold-rolled material. Strain rate change as well as short-term and longer-term creep tests were conducted. Microstructure and texture were characterized using OIM, TEM, and XRD. Deformation mechanism, in particular long-term creep, will be discussed.

10:10 AM Break

10:25 AM
Alloying Development and Microstructure Stability in High-Temperature Mo-Si-B System: *Ridwan Sakidja*[1]; John H. Perepezko[1]; [1]University of Wisconsin-Madison

Mo-Si-B alloys have been considered as potential high temperature structural materials due to their high melting points (above 2000°C) and excellent high-temperature oxidation resistance attributed to their self-healing characteristics. In the current study, the effect of alloying additions such as Ti and Cr to lower the overall weight density has been examined. The microstructure stability with the alloying additions is due to the stability of the high melting ternary-based T2 borosilicide phase.

10:50 AM
In-Situ Fracture Studies and Modeling of the Toughening Mechanism Present in Wrought LCAC, TZM< and ODS Molybdenum Flat Products: *Brian Vern Cockeram*[1]; Kwai S. Chan[2]; [1]Bechtel-Bettis; [2]Southwest Research Institute

Fractographic Examiantions of tensile and fracture toughness specimens from wrought LCAC unalloyed, ODS, and TZM molybdenum have indicated that these alloys exhibit a ductile laminate toughening mechanism that is characterized as thin sheet toughening. In-situ examinations of fracture toughness specimens using a DISMAP method provide information on the stress-intensity values needed for crack propagation, path of crack propagation, and localized measurements of strain at the crack tip. C-scan measurements confirm that delaminations occur at the crack tip, and the development of the delamiantion zone with increasing stress-intensity is determined. A micromechanical model is developed to relate the toughness values to the features of the microstructure. Molybdenum alloys with a finer grain size, such as ODS molybdenum, are shown to exhibit higher toughness values at lower temperatures. The improvement in DBTT with respect to microstructural features is understood in terms of the thin sheet toughening mechanism.

11:15 AM
Electron-Beam and Laser Welding Techniques for Refractory Alloys: *Dean M. Paxton*[1]; D. J. Senor[1]; A. Jones[1]; T. A. Delucchi[2]; [1]Pacific Northwest National Laboratory; [2]Cogema Engineering

An established electron-beam and laser welding capability at the Hanford Site recently was incorporated into the Pacific Northwest National Laboratory. In the past, electron-beam and laser welding techniques were developed and qualified for a variety of refractory alloys and other materials of interest for space reactor applications. These techniques were used for a variety of applications related to space reactor materials research including fabrication of pressurized biaxial creep test specimens. Many of these materials were subsequently subjected to irradiation testing in FFTF and EBR-II. The focus of this paper is the historical development and qualification of the electron-beam and laser weld techniques and an assessment of the irradiation performance of the welds using a

variety of characterization methods including metallography and radiography.

11:40 AM

A Study of Resistance Spot Welding of 50Mo-50Re (Wt%) Sheets: *Jianhui Xu*[1]; Tongguang Zhai[1]; John Farrell[2]; William Umstead[2]; Michael P. Effgen[2]; [1]University of Kentucky; [2]Semicon Associates

In this study, resistance-spot-welding was employed to pre-join refractory alloy 50Mo-50Re (wt%) sheets (0.002" and 0.005" thick). Different combinations of welding parameters, including weld current, weld time, electrode force, hold time, squeeze time, were used in resistance-spot-welding. The welding quality was evaluated by tensile-shear tests and microstructure examination. It was found that the strength of these welds was enhanced from 100 N to 120 N with increase in hold time from 50 ms to 999 ms, due to a higher cooling rate in the molten nugget. When the pre-weld current was linearly increased from 0 to 900 A in 8 ms, weld strength was further increased to 157 N in 0.005" samples, around 37 N higher than that of the weldment by the normally used faster heating rate. Welding defects, including porosities, columnar grains and grain boundary segregation, were also studied in these samples.

The Aluminum Fabrication Industry: Global Challenges and Opportunities: Aluminum Plenary Session

Sponsored by: The Minerals, Metals and Materials Society, Aluminum Association, TMS Light Metals Division, TMS: Aluminum Committee
Program Organizers: Subodh K. Das, Secat Inc; Michael Hal Skillingberg, Aluminum Association; Ray D. Peterson, Aleris International; Rene Kieft, Corus Group; Travis J. Galloway, Century Aluminum Company

Monday AM
March 13, 2006
Room: Theatre
Location: Henry B. Gonzalez Convention Ctr.

Session Chair: Subodh K. Das, Secat Inc

8:30 AM Plenary

The Importance of the Automotive Industry for the Future Application of Aluminium Components: *Dieter Braun*[1]; [1]Hydro Aluminium Deutschland GmbH

The need for further weight reduction of cars is a great opportunity for the Aluminium Fabricating Industry to introduce more Aluminium components for a car. Here, intelligent light weight solutions are necessary to compete with other materials. Selected examples will be presented. Additionally, to serve the Automotive Industry in a global market, especially in the fast growing markets in Asia, efficient supplying concepts are necessary. The Hydro Supplying Concept will be presented which serves the global and local demands of the Industry with selected products. Finally, examples for possible future product applications will be given.

8:55 AM Plenary

What are the Challenges and Opportunities for the Rolled Can Sheet Industry?: *Patrick M. Franc*[1]; [1]ARCO Aluminum Inc

Arco Aluminum (a subsidiary of BP N. America) has been a significant manufacturer and marketer of Aluminum rolled can sheet primarily to the beverage industry in North America for over the past 20 years. They are a joint venture owner of Logan Aluminum, an 800k ton p.a. rolling mill in Russellville Ky. Arco Aluminum develops its technology with SECAT Inc., a research and development consortium located in Lexington, KY. The current state of the RCS industry offers many challenges and opportunities for Aluminum sheet fabricators. The development of cost – competitive, sustainable solutions for current and future industry challenges as well as innovative new technology needs to begin with a fundamental understanding of value creation and enhancement along the supply chain. The creation of concepts and their development into value enhanced processes that build on these relationships will further support the long term viability of the Aluminum RCS Industry and will be the focus of this talk. The Aluminum industry continues to position itself as a material of choice to the RCS market by continuously addressing these current and future challenges and opportunities through cohesive industry partnerships and strategies.

9:20 AM Plenary

Innovations in Recycling, Continuous Casting and Rolling of Aluminum Products: *Steve Demetriou*[1]; [1]Aleris International, Inc.

Aleris International, Inc. was created with merger of IMCO Recycling, Inc. and Commonwealth Industries, Inc. on December 9, 2004. The merger established Aleris as a vertically integrated "best-in-class" aluminum recycler and sheet manufacturing company. The aluminum recycling technology combined with continuous cast technology provides the lowest cost option in making common aluminum alloy sheet for building and construction, consumer durable, transportation and distribution stocks. The combination of Aleris' direct chill ingot casting technology, with its broad alloy capabilities, and highly efficient continuous casting technology gives Aleris a competitive advantage in the market place. This talk will illustrate how the innovations in recycling, continuous casting and rolling technologies are providing the value-added products to meet customers demanding and changing needs.

9:45 AM Plenary

Driving Demand and Cost in a Global Market: *Helmut Wieser*[1]; [1]Alcoa, Inc.

Alcoa is the world's leading producer and manager of primary aluminum, fabricated aluminum and alumina facilities, and is active in all major aspects of the industry, serving the aerospace, automotive, packaging, building and construction, commercial transportation and industrial markets, bringing design, engineering, production and other capabilities to its customers. The Company's Flat Rolled Products group (which includes Mill Products and rigid container sheet) had 2004 third-party revenues of approximately $6 billion. The Company recently reorganized around 6 global businesses in order to better serve customers globally. The reorganization is designed to allow business such as the Global Mill Products group to this drive out costs as part of a global system, while working with customers to also drive demand. This discussion will illustrate key elements of Alcoa's Global Mill products business from both an operation and growth perspectives.

10:10 AM Break

10:20 AM Plenary

Innovative and Sustainable Products for the Aluminum Industry: *Kevin R. Greenawalt*[1]; [1]Novelis Corporation

Formed in January 2005 as an independent company, Novelis is comprised of the majority of the rolled products operations separated from Alcan Inc. Today, Novelis, is the global leader in aluminum rolled products and aluminum can recycling, with 36 operating facilities in 11 countries and more than 13,000 dedicated employees. This talk will describe how Novelis through its technically sophisticated and advanced production capabilities develops innovative and sustainable aluminum sheet and foil products for the automotive, transportation, beverage and food packaging, construction, industrial and printing markets.

10:45 AM Plenary

The Impact of Alloy Specifications on Aluminum Fabrication and Products - A Future View: *Thomas A. Brackmann*[1]; [1]Nichols Aluminum

As the US aluminum industry moves from primary to recycle-based raw materials, we need to examine the existing paradigm of product specification based upon the "primary metal tradition" and suggest ways to shift to an "attribute-based needs" specification which is more suited to the recycled aluminum economy. Nichols Aluminum Company, headquartered in Davenport, Iowa, is a leading manufacturer of coated and mill finish aluminum sheet for a wide variety of applications such as building and construction, transportation, machinery and equipment and consumer durable aluminum products, markets which depend sensitively on metal price and can benefit greatly from a change is paradigm. What will it take to move in this direction? This paper will examine ways and suggest strategies to make this market-driven transition.

11:10 AM Plenary

Developing Aluminum Fabrication in Chinalco: Challenge and Opportunity: *Ding Haiyan*[1]; [1]Aluminum Corporation of China

As a backbone state-owned enterprise under the direct leadership of the Central Government, Aluminum Corporation of China (Chinalco) aims to be a first-class enterprise with full vertical integration of its aluminum production assets, ranging from mining, refining, smelting and downstream fabricating. Comparing with its dominant production of alumina and primary aluminum in Chinalco, the downstream fabrication is a little small in terms of scale and capacity. In Mr. Ding's presentation, strategy and related programs on developing aluminum fabrication in Chinalco are proposed from the viewpoint of global challenge and opportunity in aluminum industry.

11:35 AM Panel Discussion

The Brandon Symposium: Advanced Materials and Characterization: Grain Boundary Theory and Experiments

Sponsored by: The Minerals, Metals and Materials Society, Indian Institute of Metals, TMS Extraction and Processing Division, TMS: Materials Characterization Committee

Program Organizers: Srinivasa Ranganathan, Indian Institute of Science; Wayne D. Kaplan, Technion; Manfred R. Ruhle, Max-Planck Institute; David N. Seidman, Northwestern University; D. Shechtman, Technion; Tadao Watanabe, Tohoku University; Rachman Chaim, Technion

Monday AM — Room: 206B
March 13, 2006 — Location: Henry B. Gonzalez Convention Ctr.

Session Chairs: Srinivasa Ranganathan, Indian Institute of Science; Wayne D. Kaplan, Technion-Israel Institute of Technology

8:30 AM Introduction to the Brandon Symposium

8:40 AM Invited

Metrics in the Five-Dimensional Angle Space for Grain Boundaries: *John W. Cahn*[1]; Jean E. Taylor[2]; [1]National Institute of Standards and Technology; [2]Courant Institute of Mathematical Sciences

Analysis of experimental data on grain boundaries (GBs) can involve putting data into angle "bins." An extreme example is Brandon's classification: if rotation angle and axis are each within 15/(sqrt n) degrees of a perfect Sigma n coincidence site lattice (CSL), the GBs are in a CSL, and not if otherwise. Other examples are studies of GB distributions in the full 5-D angle space by Saylor, et al. To determine the size of a bin (necessary for gradients), one must find a useful way, respecting symmetry, of determining metrics on the full 5-dimensional space of both misorientation and interface normal. For low-angle GBs, the issue of metric is complicated by the fact that both the rotation axes and the GB normals can stay far apart as the rotation angles approach zero. We address allthese issues, and provide a framework for choosing answers.

9:05 AM Invited

Relation between Anisotropies of Grain Boundary Energy and Segregation: *Paul P. Wynblatt*[1]; Dominique Chatain[2]; Ying Pang[1]; [1]Carnegie Mellon University; [2]CRMCN-CNRS

Results obtained on fcc alloys, by a recently developed model that allows calculation of the grain boundary (GB) energy and GB segregation as a function of the five parameters of GB orientation, will be presented. The model uses the regular solution approximation (and includes solute strain energy interactions). Some important conclusions may be summarized as follows: (a) Segregation at GB's increases with increasing GB energy; (b) The segregation profile across a GB depends on the crystallographic orientations of the two planes which terminate the crystals on the two sides of the GB. (c) The composition profile for GB's terminated by identical crystallographic planes is symmetric, but is asymmetric when GB's are terminated by different planes. (d) The strength of the segregation on one side of a GB influences the extent of segregation on the other. Experimental verification of these predictions, obtained from Nb segregation to TiO2 GB's, will be presented.

9:30 AM Invited

Special Grain Boundaries without a Coincidence Site Lattice: *Leonid A. Bendersky*[1]; John W. Cahn[1]; [1]National Institute of Standards and Technology

Special, low energy grain boundaries (GB) are said to occur whenever there is a 3-dimensional coincidence site lattice (CSL) that provides good fits of the atoms along GBs. CSL focuses on lattices, which are points, rather than on the actual atoms. There is little reason for the CSLs to be significant for GBs between crystals with large, or non-cubic, unit cells. We report here about special, large angle GBs between Al-Mn-Fe-Si grains of a cubic phase having irrational orientation relationship. The GB's have many of the other attributes of a special GB, yet there is no CSL. Motifs of the phase continue to pack across these GBs and retain orientational order, while paying little attention to the change in a lattice. These results suggest an enlarged criterion for the existence of special GBs. Variations in compositions result in the formation of quasicrystals and an unusual glass, dubbed q-glass.

9:55 AM Invited

What Does it Mean to be Special?: *Alexander H. King*[1]; Shashank Shekhar[1]; [1]Purdue University

In 1966, David Brandon introduced an ad hoc geometrical rule to categorize grain boundaries as either "special" or "general." Forty years later, the Brandon criterion is widely used and is often applied where it was never intended. We examine the assumptions of the Brandon criterion, and other criteria of "specialness." We compare their predictions with experimental data from the literature and show that the choice of a particular criterion, and of particular parameters within any criterion, should depend upon the underlying physics of the property of interest. A grain boundary that is special with respect to diffusion, for example, may not be special with respect to mechanical properties. Studies of the dihedral angles formed between "nearly special" boundaries are used to demonstrate a distinction between special and general properties, in terms of interfacial energy. Acknowledgement: This work is supported by the US Department of Energy, under Contract Number DE-FG01-01ER45940.

10:20 AM Break

10:35 AM Invited

On the Effect of Grain Boundary Junctions on Grain Growth: *Günter Gottstein*[1]; Lasar S. Shvindlerman[1]; [1]RWTH Aachen University

Grain growth in polycrystalline materials is traditionally interpreted in terms of curvature driven grain boundary motion. Recent investigations on tricrystals have provided unambiguous evidence that grain boundary triple junctions are defects on their own with specific thermodynamic and kinetic properties. As a consequence they can exert a substantial drag on grain growth kinetics and thus, microstructure and texture evolution. Since the strength of junction drag does not only depend on the ratio of triple junction and grain boundary mobility but is also proportional to the grain size, this effect is expected to be particularly pronounced in ultra fine grained and nanocrystalline materials. At very strong junction drag the grain growth kinetics can be entirely controlled by junction kinetics. This does not only affect the instantaneous grain growth rate but also causes a conspicuous retardation of the grain growth rate during subsequent annealing under conditions where grain boundary kinetics prevail.

11:00 AM Invited

Grain Boundary Character and Dopant Effects of Oxide Ceramics: *Yuichi Ikuhara*[1]; [1]University of Tokyo

Bicrystal-experiments have an advantage to be performed because grain boundary character and the kind of dopants can be controlled, and the fabricated boundaries are easily treated for the subsequent characterization. We have systematically fabricated the bicrystals for Al2O3 and ZrO2 so as to include low angle, CSL and high angle grain boundaries to cover all types of grain boundaries. In addition, several dopants such as Y2O3, SiO2 were doped for the fabricated bicrystals. The atomic structures, chemistry and energy of the grain boundaries in the respective bicrystals were investigated by HREM, HAADF-STEM, EDS, EELS and thermal grooving techniques. It was found that the grain boundary structures and ener-

gies strongly depend on the grain boundary characters and the kinds of dopants. In addition, the most stable grain boundary structures were theoretically calculated by the static lattice and molecular orbital calculations to compare with the experimentally obtained results.

11:25 AM Invited

Grain Boundary Engineering by Magnetic Field Application: *Tadao Watanabe*[1]; Sadahiro Tsurekawa[1]; Xiang Zhao[2]; Liang Zuo[2]; Claude Esling[3]; [1]Tohoku University; [2]Northeastern University; [3]University of Metz

A new approach to the grain boundary engineering for advanced materials has been recently proceeded by using different processing methods under a magnetic field. The advent of a helium-free superconducting magnet and the orientation imaging microscopy (OIM) has enabled us to develop such new processing methods of the grain boundary engineering for high performance materials. Recent experimental works on nanocrystalline nickel, iron alloys and steels have demonstrated that magnetic annealing, magnetic crystallization from the amorphous state and magnetic phase transformation under a high magnetic field, have a high potential for development of advanced materials and can produce various unique microstructures which can be the origins of high performance and desirable bulk properties, and cannot be produced by presently existing processing methods.

11:50 AM Invited

Magnetically Controlled Grain Boundary Motion and Microstructure Evolution in Non-Ferromagnetic Metals: *Dmitri A. Molodov*[1]; [1]RWTH Aachen University

The current research on grain boundary dynamics, texture and grain structure development in high magnetic fields will be reviewed. Grain boundary motion can be affected by a magnetic field, if the anisotropy of the magnetic susceptibility generates a gradient of the magnetic free energy density across the boundary. The application of a magnetic field to locally deformed zinc single crystals results in growth selection, i.e. in a growth of new preferentially oriented grains. It is demonstrated for zinc and titanium sheet that a magnetic driving force superimposed to a capillary driving force can bias the microstructure evolution during grain growth with regard to grain size and crystallographic texture. A theoretical analysis of grain growth kinetics in the presence of an external magnetic field predicts that magnetically affected grain growth will result in a change of the grain orientation distribution in favour of grains with a lower magnetic free energy density.

12:15 PM

Exploring the Structure of Asymmetrical Tilt Grain Boundaries in Gold: *J. Anthony Brown*[1]; Douglas L. Medlin[2]; Yuri Mishin[1]; [1]George Mason University; [2]Sandia National Laboratories

Results of atomistic simulation studies of <110> 90° asymmetrical tilt grain boundaries (GBs) in gold are presented and compared with HRTEM observations of the same boundaries. The structure of interfacial disconnections associated with the {111}/{112} boundary that accommodate coherency strains at this interface has been investigated in great detail. The stress accommodation at other GBs of the <110> 90 deg series has also been explored through the range of inclination angles between the {111}/{112} interface and the symmetrical {557}/{557} GB. The results are interpreted in terms of the formation of facets, disconnections, and the emission of intrinsic stacking faults into the bulk. This study presents a clarification of the role of coherency strains and disconnections in the structure of asymmetrical GBs in metals. The combination of atomistic modeling and experiment leads to a better understanding of asymmetrical GBs and their possible role in mechanical behavior of metals.

The Rohatgi Honorary Symposium on Solidification Processing of Metal Matrix Composites: Overview of Developments in Cast MMCs

Sponsored by: The Minerals, Metals and Materials Society, TMS Materials Processing and Manufacturing Division, TMS Structural Materials Division, TMS/ASM: Composite Materials Committee, TMS: Solidification Committee

Program Organizers: Nikhil Gupta, Polytechnic University; Warren H. Hunt, Aluminum Consultants Group Inc

Monday AM
March 13, 2006

Room: 207B
Location: Henry B. Gonzalez Convention Ctr.

Session Chairs: Krishan K. Chawla, University of Alabama; Nikhil Gupta, Polytechnic University

8:30 AM Introductory Comments: A brief introduction to the life and work of Dr. Rohatgi

8:45 AM Invited

Opportunities and Challenges in Cast Metal Matrix Composites: *Pradeep Kumar Rohatgi*[1]; Atef Daoud[2]; Nikhil Gupta[3]; Rajiv Asthana[1]; [1]University of Wisconsin; [2]Central Metallurgical Research and Development Institute; [3]Polytechnic University

The present work reviews the historical evolution of Cast Metal Matrix Composites (MMCs), which can be produced in foundries. After a brief introduction on the structure, solidification and processing of composites, the possible effects of reinforcements on solidification are discussed, including a reduction in microsegregation of solute and concentration of particles in the interdendritic regions due to particle pushing phenomenon. This is followed by some applications of MMCs, which include automotive and space applications. Cast MMCs that are being currently developed are also discussed; these include Aluminum and Magnesium based MMCs, Lead free Copper-Graphite, and Composite Foams. Future research needs in Cast MMCs are also discussed and a possible scenario of extending the present cast MMC technology to manufacture higher performance and lower cost composites and advanced materials such as functionally gradient materials, nanocomposites, biomedical composites, smart composites, superconducting composites and porous and cellular metals, is presented.

9:10 AM Invited

Cast Aluminum Composite Applications and Barriers to Volume Production: *David J. Weiss*[1]; [1]ECK Industries Inc

Many important components for the transportation and industrial markets are produced as castings. The flexibility of the casting process and the many casting techniques available make the use of castings economically viable over a wide range of volumes. Aluminum metal matrix composite castings are used in a number of niche applications in the electronics, commercial braking and metrolgy markets but have never found a wide market. This paper discusses a number of successful applications and discusses the barriers that currently prevent more extensive use of cast aluminum metal matrix composite castings. Recent technical breakthroughs and suggestions for further work are discussed.

9:35 AM Invited

Hollow Particle Filled Lightweight Composites: *Nikhil Gupta*[1]; [1]Polytechnic University

Hollow particle filled advance composite materials have potential for being used in a variety of applications that include aircraft and spacecraft structures, ship and boat structures and buildings. A comparison of mechanical properties of metal, polymer and ceramic matrix hollow particle filled syntactic composites is presented. Fly ash cenospheres and glass microballoons are used as hollow particles in synthesizing syntactic composites. Particle size, volume fraction and wall thickness are some of the common approaches of modifying the properties of syntactic foams. A comparative study of the effectiveness of these approaches in modifying material properties of syntactic foams is carried out. The material micro-

structure, specific strength and energy absorption characteristics of these materials are discussed.

10:00 AM Invited
Synthesis of Stir Cast Aluminum Alloy Matrix Composites-Indian Contributions: *Satyanarayana Gundappa Kestur*[1]; Marimuthu Raman Pillai[2]; Bellembettu Chandrasekhar Pai[2]; Pradeep Kumar Rohatgi[3]; [1]Federal University of Parana; [2]Regional Research Laboratory, CSIR; [3]University of Wisconsin

Cast aluminum matrix composites with discontinuous dispersoids have been most favored new millenium advanced engineering material. Solidification route is the most attractive processing method with India taking the lead. Different casting processes, size and shape of dispersoids, melt treatments and heat treatment are employed to achieve better properties with resulting microstructures to be a function of these parameters. Indian researchers with initiative from Prof. Rohatgi have a major share in the development of the stir cast technique, the most simple and economical solidification route for metal matrix composite. Many challenges are involved in this synthesis. Also, laboratory scale technologies are developed in India with microstructure and properties comparable with those of commercially available MMCs abroad. This paper highlights the scientific contributions made by Indian Scientists in the development of Science and Technology of cast aluminum matrix composite, which include mixing, wettabilty of dispersoids, melt and surface treatments, and interface reaction.

10:25 AM Break

10:40 AM Invited
In-Situ Processing of Lightweight Alloy Composites: *Ramana G. Reddy*[1]; [1]University of Alabama

A new in-situ processing method for production of lightweight alloys matrix with ceramic particles reinforcements is discussed. Successful in-situ formation of Al and Mg alloys with ceramic particles (i.e. SiC, AlN) composites by bubbling reactive gas (i.e. methane, nitrogen, ammonia) into Al and Mg alloy melts was discussed. Effect of processing parameters on the formation of AlN and SiC composites was investigated. The SiC formation rate increased with decrease in the bubble size. The composites contained up to 30 wt% SiC. Kinetic rate equations of in-situ formation of composites were developed. The productions of composites by molten metal technology were discussed.

11:05 AM
Solidification Microstructures of Hybrid Aluminum Matrix Composites: *B. C. Pai*[1]; T. P. D. Rajan[1]; S. G. K. Pillai[1]; R. M. Pillai[1]; [1]Regional Research Laboratory, CSIR

Hybrid Metal Matrix Composites (HMMC) are second-generation metallic composites, where more than one type, shape and size of reinforcements are introduced into the matrix alloy. Presence of more reinforcements gives much superior properties due to synergistic effects. HMMC provides enhanced structural, mechanical and tribological properties than conventional alloys and mono composites depending upon the constituent materials. Among the various processing methods available for the fabrication of HMMC, the solidification route is preferred due to its ease of fabrication and cost effectiveness. The most common solidification technique used is the liquid metal stir casting followed by shaping using gravity, investment, pressure, squeeze and centrifugal casting methods. The solidification microstructure of these cast hybrid metal matrix composites plays an important role in determining the physical, mechanical and tribological behaviour of the composites. Hence, an understanding of solidification microstructures in HMMC becomes more vital.

11:30 AM
Developments in Science and Technology of Cast Aluminium Matrix Composites - An Overview: *Satyanarayana Gundappa Kestur*[1]; Marimuthu Raman Pillai[2]; Chandrasekhara Bellembettu Pai[2]; Pradeep Kumar Rohatgi[3]; Jeongkyon Kim[3]; Mahesh Kestursatya[4]; [1]Federal University of Parana; [2]Regional Research Laboratory, CSIR; [3]University of Wisconsin; [4]Hewlig Carbon Products

During the last three decades, substantial R&D efforts in the area of metal matrix composites have been directed to understand their processing, structure-properties as well as potentials and limitations invoking the principles of different areas such as casting/solidification, physical metallurgy, stress analysis, etc. This paper focuses mainly on some market, the quality, the intellectual property rights, cost aspects and the selection criteria for matrix and reinforcements as well as some developments taking place both in theoretical and experimental aspects of processing and structure-property correlation along with the some application aspects of cast aluminum based composites. The gaps existing for greater acceptance and commercialization as well as comparison of all aspects of cast composites in the developed countries and India are brought out in totality to take stock of the developments in science and technology with a view to strive for faster growth of applications of cast Al composites.

11:55 AM
Composite Development Activity at NPL: *Anil Kumar Gupta*[1]; Rajiv Sikand[1]; Rakesh B. Mathur[1]; Tasreem L. Dhami[1]; [1]National Physical Laboratory

The National Physical Laboratory has been engaged in undertaking systematic research on the development of wide varieties of composite materials, such as, Metal Matrix Composites, Carbon-Carbon Composites, Carbon fiber reinforced plastic composites. The developmental work includes processing, characterization and their possible applications. The emphasis has been on synthesis and secondary processing of Metal Matrix Composites and high modulus structural components. Different MMC materials have been developed using stir-casting, spray formed and Powder Metallurgy route and have been secondary processed employing hot extrusion and forging using 500 ton vertical hydraulic press. Carbon-Carbon Composites are light weight, high strength, high stiffness, low coefficient of thermal expansion, high thermal conductivity material. In addition to low recession in high temperature environment, it has capability to withstand high temperatures upto 3000C in inert atmosphere. The talk will highlight some of the important aspects related to processing, characterization and possible applications.

Ultrafine Grained Materials - Fourth International Symposium: Fundamentals of Ultrafine Grained Materials

Sponsored by: The Minerals, Metals and Materials Society, TMS Materials Processing and Manufacturing Division, TMS Structural Materials Division, TMS/ASM: Mechanical Behavior of Materials Committee, TMS: Shaping and Forming Committee
Program Organizers: Yuntian T. Zhu, Los Alamos National Laboratory; Terence G. Langdon, University of Southern California; Zenji Horita, Kyushu University; Michael Zehetbauer, University of Vienna; S. L. Semiatin, Air Force Research Laboratory; Terry C. Lowe, Los Alamos National Laboratory

Monday AM — Room: 217D
March 13, 2006 — Location: Henry B. Gonzalez Convention Ctr.

Session Chairs: Yuntian T. Zhu, Los Alamos National Laboratory; Dieter Wolf, Argonne National Laboratory; Evan Ma, Johns Hopkins University; Marc A. Meyers, University of California

8:30 AM Introductory Comments

8:35 AM Invited
Dislocation Structures in Cyclically Loaded Ultra Fine-Grain Copper: Kai Zhang[1]; Xiaozhou Liao[2]; *Julia R. Weertman*[1]; [1]Northwestern University; [2]University of Chicago

Previous experiments have shown that cryogenically-rolled UFG Cu subjected to cyclic loading undergoes significant softening, grain growth, and the development of surface extrusions/intrusions. In the present talk the dislocation structure that develops during cycling is analyzed and related to the changes that evolve in the fatigued material. Research sponsored by US DOE Grant #DE-FG02-02ER46002.

8:55 AM Invited
Dislocation and Grain-Boundary Processes during Deformation and Grain Growth in Nanocrystalline Materials by Molecular Dynamics Simulation: *Dieter Wolf*[1]; [1]Argonne National Laboratory

Molecular-dynamics simulations have been used to elucidate the deformation and grain-growth behavior of nanocrystalline fcc metals. These simulations have now become large and sophisticated enough where they begin to provide novel, materials-physics based insights into the intricate interplay between dislocation and grain-boundary processes controlling the thermo-mechanical behavior of these materials. In particular, such simulations now capture, with atomic-level resolution, the entire range of grain sizes in which the experimentally suggested transition from a dislocation-based deformation mechanism to one involving grain-boundary processes takes place as the grain size approaches dimensions of the order of tens of nanometers. By investigating the intricate coupling between grain growth and grain-boundary diffusion creep, these simulations also provide insight into the dislocation and grain-boundary processes that control the high-temperature stability of these materials. Work supported by the U.S. Department of Energy, Basic Energy Sciences-Materials Sciences, under Contract W-3l-l09-Eng-38.

9:15 AM Invited

An In Situ TEM Study of Dislocation Behavior in Nanocrystalline Copper Alloys with Different Stacking Fault Energies: *Thomas J. Balk*[1]; Yong Hao Zhao[2]; Yuntian T. Zhu[2]; Zenji Horita[3]; Terence G. Langdon[4]; [1]University of Kentucky; [2]Los Alamos National Laboratory; [3]Kyushu University; [4]University of Southern California

In nanocrystalline materials, both the nucleation and glide of dislocations are subjected to strong constraints. This study aims to uncover details of dislocation nucleation and motion within nanocrystalline materials by in-situ mechanical testing in the transmission electron microscope (TEM). High-pressure torsion and cold rolling were used to produce flat sheets of nanocrystalline copper (70 nm grain size), bronze (25 nm) and brass (13 nm). The resultant grain size was found to scale with the stacking fault energy of each material, and these two factors therefore simultaneously affect dislocation behavior within the ultrafine grains. Each metal/alloy was subjected to uniaxial tension testing in the TEM, during which the deformation microstructure was continuously observed. This talk will discuss the relative roles of dislocation emission versus deformation twinning in these copper-based materials, as well as the evolution of dislocation density, which affects the work hardening and therefore the ductility of each material.

9:35 AM

Deformation Induced Grain Growth and Softening in Electrodeposited Nanocrystalline Ni Film: *Yuntian T. Zhu*[1]; Shenggao Hong[2]; Xiaodong Chris Li[2]; Xiaozhou Liao[3]; Ruslan Z. Valiev[4]; Amiya Mukherjee[5]; [1]Los Alamos National Laboratory; [2]University of South Carolina; [3]University of Chicago; [4]Ufa State Aviation Technical University; [5]University of California

This paper reports deformation induced grain growth in electrodeposited nanocrystalline Ni film during high pressure torsion (HPT). Grain growth has been experimentally observed in nanocrystalline and ultrafine-grained Al and Cu under the deformation mode of indentation, but not under any other deformation mode. In this study, nanocrystalline Ni films produced by electro-deposition were subjected to high-pressure torsion (HPT) and grain growth was found subsequently. The HPT deformation also led to lower hardness and lower elastic modulus, which are attributed to the reduction of internal stress and change of texture. High stress and severe plastic deformation are believed required for the grain growth and the final grain size is determined by the deformation parameters.

9:50 AM

Rate-Controlling Deformation Mechanism of Electrodeposited Nanocrystalline Ni: *Yinmin (Morris) Wang*[1]; Alex V. Hamza[1]; Evan Ma[2]; [1]Lawrence Livermore National Laboratory; [2]Johns Hopkins University

Commercially available electrodeposited nanocrystalline Ni with grain sizes below 100 nm is a wide-used material to investigate the deformation and failure mechanisms of nanostructured materials. More recently attention has been focused on the rate-controlling deformation mechanisms of these materials. Repeated transition tests were applied to extract the activation volume and strain rate sensitivity of nanocrystalline Ni at different deformation temperatures. The magnitudes of these deformation parameters obtained from our experimental data indicates that unlike many models proposed in the literature, the grain boundary diffusion controlled process such as Coble creep is not a dominant deformation mechanism for the deformation temperature studied. Other possible mechanisms involved in these deformation processes are suggested. This work was performed under the auspices of the U.S. Department of Energy by University of California, Lawrence Livermore National Laboratory under contract of No.W-7405-Eng-48. Y.M. Wang acknowledges the support of Graboske Fellowship at Lawrence Livermore National Laboratory.

10:05 AM

Measurements of Vacancy Type Defects in SPD Deformed Nickel: Gerd Steiner[1]; Erhard Schafler[1]; Elena Korznikova[2]; Michael Kerber[1]; *Michael Josef Zehetbauer*[1]; [1]University of Vienna; [2]Ufa State Aviation Technical University

Ni of different purities between 99.9x% and 99.99x% have been deformed by various paths of ECAP and HPT. Results have been compared with investigations by conventional deformation (rolling, compression). In order to conclude the concentration of vacancy type lattice defects, annealing resistometry and calorimetry have been performed and combined with X-ray diffraction Bragg profile analyses. While the first two methods are sensitive to both vacancies and dislocations, the latter determines the dislocation density solely so that the vacancy concentration can be found by proper combination of results[1]. Similarly to Cu, the vacancy concentrations measured from SPD are definitely higher than those from conventional plastic deformation. The resulting vacancy concentrations are discussed in terms of their dependencies on the deformation strain, the deformation mode, the hydrostatic pressure and the purity of Ni used. [1]E.Schafler, G.Steiner, E.Korznikova, M.Zehetbauer, TMS 05, Mater.Sci Eng. A, accepted.

10:20 AM

Deformation Twinning Mechanisms in Nanocrystalline Ni: *Xiao-Lei Wu*[1]; En (Evan) Ma[2]; Ke Lu[3]; [1]Institute of Mechanics, Chinese Academy of Sciences; [2]Johns Hopkins University; [3]Institute of Metal Research, Chinese Academy of Sciences

Twinning has recently been identified as a contributing plastic deformation mechanism in nanocrystalline (nc) metals. When nc metals are forced to deform to large strains, in the deforming nanostructure there will inevitably be build up of local stress concentrations that are at sufficient levels for deformation twinning to become a competitive response. In the present paper, we studied deformation twinning mechanisms in nc-Ni severely deformed by the surface mechanical attrition treatment and ball milling. Extensive HREM examinations confirmed that twinning does occur upon large plastic deformation in nc Ni. The heterogeneous and homogeneous twinning mechanisms included 1) the nucleation at the grain boundary and growth (lengthening and thickening) into the grain interior via partial dislocation emission, 2) dynamic overlapping of stacking faults on adjacent planes, and 3) the dissociation of an initial segment of the high angled grain boundary and its subsequent migration to producing the twin lamella.

10:35 AM Break

10:50 AM Invited

Simultaneously Achieving High Strength, Strain Hardening, and Large Plasticity in Ultrafine-Grained Bulk Alloys: *Evan Ma*[1]; [1]Johns Hopkins University

Bulk ultrafine-grained or nanostructured metals/alloys, prepared via severe plastic deformation for example, usually exhibit a high strength. But sometimes this advantage comes at the expense of plasticity. Even for cases where both high strength and large plastic strains are attained, the material often lacks the strain hardening capability needed to sustain uniform elongation in tensile deformation. For elemental metals, we have discusses a number of ways to improve strain hardening, at previous conferences. Here we discuss one of the strategies for alloys, using a model bulk Ti-based alloy made via chill casting. The origin of the high strength and the dislocation pile-up, the extensive dislocation slip and their interactions responsible for the obvious strain hardening to large strains, the alloy/microstructure design recipe, and the one-step bulk processing protocol, will be discussed. This work was performed in collaboration with the MANS research team (SYNL) and Dr. J. Eckert's group (DTU).

11:10 AM Invited
Possibility to Manage Both Strength and Ductility in Ultrafine Grained Structural Metallic Materials: *Nobuhiro Tsuji*[1]; [1]Osaka University

One of the problems of ultrafine grained metallic materials is limited uniform elongation contrary to high strength. The issue is discussed on the basis of the author's original evidences. The limited uniform elongation is due to early plastic instability caused by limited strain-hardening capability in the ultrafine grained microstructures. One of the ways to manage both high strength and adequate ductility is to increase the strain-hardening rate by any means, such as by dispersing nano precipitates/particles. A successful example is the multiphased nano-structure composed of submicrometer ferrite grains and nano carbides in the low carbon steel fabricated by a special thermomechanical treatment starting from martensite structure. Another possibility has been found recently in some aluminum alloys which showed unexpected increase in elongation as the SPD strain increased. The mechanism is discussed from a viewpoint of strain rate sensitivity of the ultrafine grained materials.

11:30 AM Invited
Mechanisms of Grain-Size Refinement and Plastic Deformation in Ultra-Fine-Grained Metals: *Marc A. Meyers*[1]; [1]University of California, San Diego

The evolution of the microstructure leading from conventional polycrystaline to submicrometer sized grains is described in terms of the break up of the existing grains and grain-boundary rotations at the latter stages, leading to an equiaxed structure. The analogies between the structure generated within adiabatic shear bands and ECAP are drawn, with attention to the Zener parameter. Plastic deformation mechanisms operating in the ultrafine grain size domain are reviewed and compared with nanocrystalline and conventional polycrystalline aggregates. Research Support: DMR 0419222; CMS 0210173(NIRT).

11:50 AM Invited
Mechanical Behavior of Individual Grains in Nanocrystalline Ni during Tensile Deformation: *Zhiwei S. Shan*[1]; Andy Minor[2]; Jorg M. K. Wiezorek[3]; David M. Follstaedt[4]; James Knapp[4]; Eric Stach[5]; Oden L. Warren[6]; Scott X. Mao[3]; [1]University of Pittsburgh and NCEM, LBL; [2]NCEM, LBL; [3]University of Pittsburgh; [4]Sandia National Laboratories; [5]Purdue University; [6]Hysitron, Inc.

Ever since the concept of nanocrystalline (nc) materials was proposed, it has been thought that the grain boundary (GB) structure of nc materials is different from that of their coarse-grained counterpart and that the unique properties of nc materials result mainly from this difference. However, increasing evidence shows that the GB structure of nc materials is similar to their coarse-grained counterpart. This naturally leads to the following question: do individual nano grains behave differently during deformation from what has been expected? In this work, nano beam electron diffraction has been used to study the behavior of individual grains in nc Ni during deformation. Large variations in the magnitude of grain rotation were found. Moreover, direct measurement of lattice distortions during straining reveals that grain interiors may experience large elastic distortions during tensile deformation. Implications of these experimental findings for the deformation behavior of nc materials are discussed.

12:10 PM Invited
Deformation Analysis of Strain Hardening and Softening Materials during Equal Channel Angular Pressing: *Hyoung Seop Kim*[1]; [1]Chungnam National University

From the viewpoint of grain refinement by severe plastic deformation, the processing temperature generally needs to be as low as possible. However, ECAP at elevated temperatures is inevitable for hard-to-deform materials to prevent fracture during the processing. Material deformation characteristics to be noted at higher temperatures are strain softening (decreasing flow stress with increasing strain) and higher strain rate sensitivity, which were particularly important in the degree of inhomogeneous deformation. Strain hardening response of a workpiece material highly affects plastic flow behaviour during ECAP; a larger corner gap and the inhomogeneous strain distribution.In the present study, deformation behavior of strain hardening and strain softening materials during ECAP is investigated using the finite element method. The predicted deformation homogeneity is compared to the experimental results of Al alloys at room temperature, Ti alloy at high temperature and plasticine polymer.

Wechsler Symposium on Radiation Effects, Deformation and Phase Transformations in Metals and Ceramics: Irradiation Effects

Sponsored by: The Minerals, Metals and Materials Society, ASM International, TMS Structural Materials Division, ASM Materials Science Critical Technology Sector, TMS Materials Processing and Manufacturing Division, TMS/ASM: Mechanical Behavior of Materials Committee, TMS/ASM: Nuclear Materials Committee, TMS/ASM: Phase Transformations Committee
Program Organizers: Korukonda L. Murty, North Carolina State University; Lou K. Mansur, Oak Ridge National Laboratory; Edward P. Simonen, Pacific Northwest National Laboratory; Ram Bajaj, Bettis Atomic Power Laboratory

Monday AM — Room: 208
March 13, 2006 — Location: Henry B. Gonzalez Convention Ctr.

Session Chairs: K. Linga Murty, North Carolina State University; Louis K. Mansur, Oak Ridge National Laboratory

8:30 AM Introductory Comments

8:55 AM Keynote
Then and Now with Radiation Effects, Deformation, and Phase Transformations: *Monroe S. Wechsler*[1]; [1]North Carolina State University

Research in radiation physics and materials science is, by its very nature, a forward-looking enterprise, but sometimes it may be worthwhile to review past developments and suggest where further work needs to be done. In this short review, we briefly discuss martensite crystallography, the shape memory phenomenon, and some radiation-effects topics, i.e., radiation hardening and embrittlement, impurity-defect interactions, and calculations of the production of displacements, helium, hydrogen and transmutation products in fission neutron and accelerator-driven spallation systems.

9:30 AM Invited
Point Defect Interactions in Fe-Cr Alloys: Jae-Hyeok Shim[1]; Kwan L. Wong[2]; *Brian D. Wirth*[2]; [1]Korea Institute of Science and Technology; [2]University of California

Fe-Cr alloys are a leading candidate material for Generation IV and Fusion reactors. Complete understanding of the response of Fe-Cr alloys to irradiation requires knowledge of point defect and point defect cluster interactions with Cr solute atoms and impurities. In this work, we have used two different Finnis-Sinclair type potentials for Fe-Cr alloys. The potentials predict different interactions between Cr and self-interstitial defects. Results of atomistic molecular dynamics and kinetic Monte Carlo simulations to investigate the point defect behavior in Fe-Cr alloys are presented as a function of Cr content and the character of Cr interactions with self-interstitial defects. The modeling results are compared to experiments performed by Maury and co-workers to investigate the isochronal annealing recovery of electron irradiated Fe-Cr. The results provide insight into the effect of Cr atoms on self-interstitial cluster behavior and indicate potential is more accurate for describing point defect – Cr interactions.

9:55 AM
The Effects of Helium and Hydrogen in Irradiated Single Crystal Body-Centered Cubic Iron: *Maria A. Okuniewski*[1]; Chaitanya S. Deo[2]; Srivilliputhur G. Srinivasan[2]; Michael I. Baskes[2]; Michael R. James[2]; Stuart A. Maloy[2]; James F. Stubbins[1]; [1]University of Illinois at Urbana-Champaign; [2]Los Alamos National Laboratory

Ferritic-martensitic steels are candidate structural materials for Generation IV reactors, fusion systems, and accelerator driven systems (ADS). These steels have been selected due to their resistance to void swelling, irradiation creep, and helium (He) and hydrogen (H) embrittlement at higher temperatures. During fusion or ADS reactor operations the structural materials will be subjected to displacement damage, as well as gen-

eration of He and H via (n,a) and (n,p) transmutation reactions, respectively. A systematic study utilizing both simulation and experimental methods has been carried out to examine the effects that He and H have on irradiated single crystal body-centered cubic iron. Molecular dynamics was used to study the effects of incident ion energies, He and H concentrations and the temperature on the evolution of defects. The modified embedded atom method was used to describe the interatomic interactions. The experimental studies employed positron annihilation spectroscopy and transmission electron microscopy for defect characterization.

10:15 AM

Kinetics of the Migration and Clustering of Helium and Hydrogen during Spallation Reactions in bcc Iron: *Chaitanya S. Deo*[1]; Maria A. Okuniewski[2]; Srinivasan G. Srivilliputhur[1]; Michael I. Baskes[1]; Stuart Andrew Maloy[1]; Michael R. James[1]; James Stubbins[2]; [1]Los Alamos National Laboratory; [2]University of Illinois

Spallation refers to nuclear reactions that occur when energetic subatomic particles (such as protons in an accelerator beam) strike or interact with the nucleus of an atom (such as in a target) in which many particles, including many neutrons, are ejected from the nucleus. High levels of transmutation products such as H and He are produced in spallation reactions in structural materials such as bcc ferritic steels. We investigate the defect production energetics, defect mobility, and cluster properties of the Fe-He system using a combination of molecular dynamics and kinetic Monte Carlo (kMC) calculations. The kMC results illustrate the competition of the vacancies and clusters as sinks for the interstitial He in the system and as possible nucleation sites for bubbles. Order kinetics of transmutation gas mechanisms are studied with the kMC method and analyzed using diffusion limited reaction rate theory.

10:35 AM Break

10:55 AM

Kinetics of Coarsening of Helium Bubbles during Implantation and Post-Implantation Annealing.: *Stanislav Golubov*[1]; Roger Stoller[1]; Steve Zinkle[1]; [1]Oak Ridge National Laboratory

To understand the effects of He on irradiated metals requires modeling of helium-vacancy clusters evolution. Recently, a new method of solving the two-dimensional master equation describing He-vacancy cluster evolution has been applied to calculate bubble evolution in a stainless steel irradiated with alpha particles near room temperature and annealed in the temperature range of 600-900ºC. For the first time, the evolution of the helium bubble size distribution function was precisely calculated in 2D phase space and good agreement with experimental results was obtained. The results indicate that: Brownian motion of bubbles via surface vacancy diffusion provides a reasonable explanation of bubble evolution, most bubbles are near the equilibrium state at T>700ºC, lack of vacancies at temperatures lower than about 700°C leads to a decrease in bubble growth, and use of a non-ideal He equation of state influences bubble density and swelling, both are higher than for the ideal gas case.

11:15 AM

Review of Primary Damage Production in Iron: *Roger E. Stoller*[1]; [1]Oak Ridge National Laboratory

Results of extensive investigations of primary damage formation in iron using molecular dynamics (MD) displacement cascade simulations in iron will be reviewed. The database of MD cascades includes energies from near the displacement threshold to 200 keV and temperatures from 100 to 900K. The review will focus on the role of cascade energy and temperature in primary damage formation. Damage production is characterized in terms of the total number of point defects produced, the partitioning of the this total into isolated and clustered defects, and the size distributions of the interstitial and vacancy clusters. The database primarily includes cascades produced in perfect material, with the impact of pre-existing damage and free surfaces evaluated for a limited number of conditions. The applicability of the atomistic simulations for evaluating neutron energy spectrum effects in different irradiation conditions (fission, fusion, spallation) will also be discussed.

11:35 AM

The Thermal Annihilation Process of Stacking Fault Tetrahedra: *Yoshitaka Matsukawa*[1]; Stanislav I. Golubov[1]; Bachu N. Singh[2]; Steven J. Zinkle[1]; [1]Oak Ridge National Laboratory; [2]Risø National Laboratory

Thermal stability and annihilation of defect clusters are fundamental issues necessary to understand the kinetics of defect microstructure evolution under irradiation. The stacking fault tetrahedron is a common defect cluster directly produced during neutron irradiation in fcc metals. The objective of the present study is to identify the mechanism of thermal annihilation of SFTs at various sizes by in situ annealing in a transmission electron microscope (TEM). Various sizes of SFTs (<2~50nm) were introduced into gold by quenching from high temperatures. Also, small SFTs (≈2nm) were introduced into gold, copper, silver, nickel, and aluminum thin foils (<50nm) by Kiritani's high-speed deformation method. Annihilation temperature strongly depended on SFT size. A medium-sized SFT (10nm) in quenched gold was observed to annihilate at 938K, whereas a large SFT (40nm) disappeared at 1010K. In both cases annihilation occurred instantaneously; neither morphological nor size changes were detected within 33ms timestep resolution.

2006 Nanomaterials: Materials and Processing for Functional Applications: Nanostructure Manufacturing, Characterization and Functionalization

Sponsored by: The Minerals, Metals and Materials Society, TMS Electronic, Magnetic, and Photonic Materials Division, TMS: Nanomaterials Committee
Program Organizers: W. Jud Ready, GTRI-EOEML; Seung Hyuk Kang, Agere Systems

Monday PM — Room: 214C
March 13, 2006 — Location: Henry B. Gonzalez Convention Ctr.

Session Chairs: Seung Hyuk Kang, Agere Systems; W. Jud Ready, GTRI-EOEML

2:00 PM Introductory Comments

2:05 PM Invited

X-Ray Nano-Diffraction of Individual Zinc Oxide Nano-Rings: Iuliana Dragomir-Cernatescu[1]; *Robert L. Snyder*[1]; Puxian Gao[1]; Zhong Lin Wang[1]; Yanan Xiao[2]; Zhonghou Cai[2]; [1]Georgia Institute of Technology; [2]Argonne National Laboratory

Nano-structures, whose lateral dimensions fall in the range of 1 to 100 nm, have received growing interests due to their outstanding proprieties and their potential applications. The development of these new structures into future nano-devices crucially depends on the development of new characterization techniques and theoretical models for a fundamental understanding of the relationship between the structure and properties. X-ray diffraction (XRD) has been successfully applied to microstructural characterization of bulk powder nano-structured materials, where useful information, such as crystallite size distribution, crystallite shapes and lattice defects were evaluated from the X-ray pattern. In the present case XRD analysis was employed for the characterization of individual ZnO nano-rings. Measurements of XRD lines from a single-crystal nano-ring were achieved by using the unique nano-diffraction facility at the APS. This new approach provides detailed information about the nano-structural parameters of individual ZnO nano-rings. The results were compared with those obtained from SEM/TEM.

2:30 PM Invited

Nanomechanical Testing and Nanomechanical Machining of Nanobuilding Blocks: *Xiaodong Li*[1]; [1]University of South Carolina

The extremely small dimensions of nanobuilding blocks, such as nanoparticles, nanotubes, nanowires, and nanobelts, impose a tremendous challenge to many existing testing and measuring techniques for experimental studies of their mechanical properties. We have developed a nanomanipulator that can be used inside a scanning electron microscope (SEM) to perform tensile, bending, creep and fatigue tests for nanobuilding

blocks. We have also extended application of traditional nanoindentation approaches to nanobuilding blocks for directly measuring their mechanical properties. Hardness, elastic modulus and fracture toughness of nanoparticles, nanowires and nanobelts were measured using a nanoindenter. Nanoscale deformation behavior and fracture mechanisms were studied by post in-situ imaging of the indents. We have developed novel nanomechanical machining methodologies and tools that are able to perform operations such as indenting, cutting, milling, shaping, forging, polishing to realize functional nanostructures and nanodevices.

2:55 PM Break

3:10 PM Invited

Manufacturing with Micro-Organisms: A New Biological/Synthetic Chemical Paradigm for the Mass Production of Functional 3-D Nanoparticle Structures: *Kenneth H. Sandhage*[1]; Sam Shian[1]; Michael R. Weatherspoon[1]; Shawn M. Allan[1]; Ye Cai[1]; Chris S. Gaddis[1]; Phillip D. Graham[1]; Michael Haluska[1]; Gul Ahmad[1]; Ben Church[1]; Robert L. Snyder[1]; Mark Hildebrand[2]; Brian P. Palenik[2]; Dori Landry[2]; [1]Georgia Institute of Technology; [2]University of California at San Diego

The widespread commercial use of three-dimensional (3-D) nanostructured devices will require fabrication protocols capable of: i) precise 3-D assembly on a fine scale and ii) mass production on a large scale. These often-conflicting requirements can be addressed with a new paradigm that merges biological self-assembly with synthetic chemistry: Bioclastic and Shape-preserving Inorganic Conversion (BaSIC). Nature provides spectacular examples of micro-organisms (diatoms, coccolithophorids, etc.) that assemble intricate bioclastic 3-D structures. Through sustained reproduction of such micro-organisms, enormous numbers of 3-D micro/nanostructures with identical morphologies may be generated. Such massive parallelism and species-specific (genetically-controlled) precision are highly attractive for device manufacturing. However, natural bioclastic chemistries are rather limited. With BaSIC, biogenic assemblies can be converted into non-natural functional chemistries (e.g., TiO2, ZrO2, BaTiO3, Zn2SiO4, polymers), while preserving the biogenic morphologies. Future genetic engineering of biomineralizing micro-organisms may be coupled with BaSIC to yield low-cost nanostructured devices with tailored shapes and tailored chemistries.

3:35 PM Invited

Novel Nanostructured Materials by Physical Vapor Deposition and Sol-Gel Techniques: *Ashutosh Tiwari*[1]; [1]University of Utah

Nanoscience and Nanotechnology represents one of the hottest frontiers in Physical Sciences and Engineering. Confinement effects due to boundary conditions make "Nanostructured Materials" behave much differently than their bulk counterparts. In this talk, I will present some of my interesting results related to these materials. Major focus will be on following three topics: (i) Nanodots for magnetic data storage (ii) Novel Superlattice Structures for low-field magnetic sensor applications (iii) Nanostructured Epitaxial thin films of Oxide-based Diluted Magnetic Semiconductors.

4:00 PM Break

4:15 PM

Field Deployable Nano-Band Electrode System for Arsenic Analysis: *David L. Cocke*[1]; Jewel A. Gomes[1]; Sudharshan Varma[1]; Bonnie Ardoin[1]; Sujith Mididuddi[1]; Hector Moreno[1]; Eric Peterson[2]; [1]Lamar University; [2]Highland Community College

Arsenic has long been an USEPA priority pollutant and is an important environmental concern because of its toxicity and carcinogenicity even at parts per billion level. It is very important to speciate its different oxidation states of arsenic for better understanding of its chemical behavior, the removal efficiency and removal mechanism. In the present work, a relatively new nano-band electrode system has been optimized for the determination of both As(III) and As(V) in water samples using Anodic Stripping Voltammetric technique. The influence of deposition potential, different supporting electrolytes and plate time on the arsenic stripping peak was investigated. A detection limit of 0.4 ppb has been obtained using USEPA method of detection limit, with plate times of just 10 seconds. The major interference was found to be from copper during measurements. Finally, the optimized system has been used for arsenic determination in real water samples, e.g. Rio Grande basin.

4:35 PM

Sensing Properties of a Novel Fe-Fe2O3/Polyoxocarbosilane Core-Shell Nanocomposite Powder Prepared by Laser Pyrolysis: Adelina Tomescu[1]; *Rodica Alexandrescu*[2]; Ion Morjan[2]; Florian Dumitrache[2]; Lavinia Albu[2]; Victor Ciupina[3]; Zdenek Bastl[4]; Ana Galikova[5]; Josef Pola[5]; [1]National Institute of Materials Physics; [2]National Institute for Lasers Plasma and Radiation Physics; [3]Ovidius University of Constanta; [4]J. Heyrovsky Institute of Physical Chemistry; [5]Czech Academy of Science

Metal oxide materials are widely used for gas sensing. Capable of operating at elevated temperatures and in harsh environments, they are mechanically robust and relatively inexpensive and offer exquisite sensing capabilities, the performance of which is dependent upon the nanoscale morphology. We report here about the synthesis and sensing properties of a thermally stable Fe-based nanocomposites prepared by continuous-wave IR laser-induced and ethylene sensitized co-pyrolysis of gaseous iron pentacarbonyl and hexamethyldisiloxane in argon. The simultaneously occurring formation of iron from iron pentacarbonyl and that of organosilicon polymer from hexamethyldisiloxane yield iron nanoparticles surrounded by organosilicon polymer shell. The particles were characterized by spectral analyses, electron microscopy, thermal gravimetry. They become superficially oxidized in atmosphere. For testing the sensing properties (sensitivity and selectivity) of the Fe/organosilicon based nanocomposites, thick films deposited on alumina substrates were heated at 450 C and the variation of their electrical resistance in presence of CO and CH4 (in dry and humid air) was measured. Preliminary results indicate a marked selectivity of the new sensor relatively to the tested toxic gases.

4:55 PM Break

5:10 PM

Synthesis and Characterization of Ag Nanorods in AAO Templates through Sol-Gel Method: Khwaja Moinuddin[1]; *Paul Keierleber*[1]; Louisa Hope-Weeks[1]; Iris V. Rivero[1]; [1]Texas Tech University

The objective of this research is to characterize the efficiency of synthesis techniques for the fabrication of Ag nanorods. Specifically, template-based methods were selected for further investigation based on the quality of its products which is characterized by yields of highly-ordered structure of monodisperse nanorods and nanotubules. Two template-based syntheses (using AAO) have been combined with sol-gel method. The first method involves preparation of a (2M) silver salt (AgNO3) solution followed by suspension of the commercially available AAO templates (pore size 0.02μm) in the solution. The second method involves preparation of a pre-reduced solution of metal salt - silver nitrate (2M), sodium citrate (2M) and sodium borohydride (2M) followed by suspension of the AAO templates in the solution. Results from these fabrication procedures were evaluated in terms of the characteristics of its products (Ag nanorods' structure and dimensions), production costs, and simplicity of replication procedure.

3-Dimensional Materials Science: 3-D Representation and Computation

Sponsored by: The Minerals, Metals and Materials Society, TMS Structural Materials Division, TMS: Advanced Characterization, Testing, and Simulation Committee
Program Organizers: Jeff P. Simmons, U.S. Air Force; Michael D. Uchic, Air Force Research Laboratory; Dorte Juul Jensen, Riso National Laboratory; David N. Seidman, Northwestern University; Anthony D. Rollett, Carnegie Mellon University

Monday PM Room: 205
March 13, 2006 Location: Henry B. Gonzalez Convention Ctr.

Session Chairs: Jeff P. Simmons, U.S. Air Force; Jaimie S. Tiley, U.S. Air Force

2:00 PM
3D Digital Microstructures with Distributions of Particles: *Anthony D. Rollett*[1]; Stephen Sintay[1]; Abhijit Brahme[1]; Joseph Fridy[2]; David Saylor[3]; [1]Carnegie Mellon University; [2]Alcoa Technical Center; [3]FDA

A method for statistical reconstruction of digital microstructures in three dimensions is described that includes orientation information as well as grain structure. Recent progress is described in developing a method for inserting small particles with variable shape into such structures. The approach is illustrated by an example of application to modeling an aerospace aluminum alloy.

2:20 PM Invited
Databases and Web Services in Support of Computational Materials: *Gerd Heber*[1]; Anthony R. Ingraffea[1]; [1]Cornell Theory Center

The datasets underlying sophisticated multi-scale and multi-physics models of 3D computational materials have grown dramatically over the last decade in both, size and complexity. The increase in size reveals scalability issues in traditionally file-based application designs, which are inadequate for applications involving (meta-) data-sharing and distributed applications (e.g., Web services, GRID). The higher complexity demands more rigorous data-modeling in form of database-, XML-, and RDF schemas, as well as domain ontologies. The challenge at hand is to create integrated environments providing access to the best available experimental data and powerful simulation and intelligent search capabilities.This is a report on ongoing efforts in the Cornell Fracture Group (CFG) to create Web portal-like environments for computational materials research. These portals offer users access (through a Web browser) to various materials resources and suites of modeling tools developed by the CFG and others.

2:45 PM Invited
Computational Models for Crystal Plasticity Simulations: *Somnath Ghosh*[1]; [1]Ohio State University

The recent years have seen a paradigm shift towards the use of crystal plasticity models to understand deformation and damage mechanisms for life prediction. In this approach, the mechanical response of polycrystalline aggregates is deduced from the behavior of constituent crystal grains. A crystal plasticity based FEM model is developed using multiple time scaling for predicting fatigue of metals and alloys in this paper. The multi-time scaling invokes compression and rarefaction of time scales to enable simulation of a large number of cycles. Methods of digital microstructure reconstruction are discussed for image based modeling. The material constitutive parameters are calibrated from experimental results and the model is validated with experiments. Creep and cyclic deformation simulations are conducted for simulating the development of local stresses, strains. Localization phenomenon is studied as a function of the microstructure.

3:10 PM
Finite Element Based Methodology for the Prediction of Mechanical Properties of Al/Sic$_p$ Composites Using Realistic Computer Simulated Microstructures: *Arun Sreeranganathan*[1]; Harpreet Singh[1]; Arun M. Gokhale[1]; [1]Georgia Institute of Technology

Finite element (FE) based simulations of micro-mechanical response are performed on computer simulated microstructures of discontinuously reinforced aluminum matrix composites that incorporates realistic complex particle morphologies/shapes, spatially non-uniform distribution of particles and anisotropic particle orientations. The simulated microstructures contain over ten thousand particles and the FE results are compared with that for real microstructures to validate the simulation model. Virtual microstructures are created by varying numerical parameters in the model and FE simulations are carried out to reflect the effect of microstructure (and therefore, processing conditions) on the mechanical response of the materials.

3:30 PM
3D Image-Based Modeling of the Effect of Microstructure on Mechanical Response: *Andrew B. Geltmacher*[1]; Alexis C. Lewis[1]; [1]Naval Research Laboratory

It is well known that the true 3D nature of microstructures strongly dictates the mechanical performance of materials. Thus, it is critical to understand the impact of real 3D microstructures in developing accurate predictive models of the performance of advanced materials. This presentation will focus on the mesoscale mechanical response of a superaustenitic stainless steel and a beta titanium alloy. This research uses 3D analysis, scientific visualization, and Finite Element Modeling (FEM) to understand the relationships between mechanical behavior and microstructural features in these materials. 3D analysis of digitally reconstructed microstructures, 3D image-based FEM simulations, and percolation analyses are performed on real 3D microstructures to track evolution of stress, strain, yield, and damage under the influence of various applied stress states, with particular emphasis on determining the types of microstructural features which serve as initiation sites of deformation and failure.

3:50 PM Break

4:10 PM
Three-Dimensional (3D) Microstructure Visualization and Finite Element Modeling of the Mechanical Behavior of Heterogeneous Materials: *Nikhilesh Chawla*[1]; Rajen S. Sidhu[1]; V. V. Ganesh[1]; [1]Arizona State University

The mechanical behavior of materials is inherently controlled by microstructure. In particular, heterogeneous materials, consisting of two or more components or phases, have complex microstructures. This makes modeling of the mechanical behavior a challenge. We have developed a three dimensional (3D) approach to (a) constructing a "virtual microstructure" in 3D by serial sectioning technique, and (b) finite element modeling using the 3D microstructure as a basis. In this talk we will explore the fundamentals of the 3D virtual microstructure modeling methodology. This methodology was used to study the deformation behavior of SiC particle reinforced metal matrix composites. The role of second phase fraction, morphology, and aspect ratio on deformation was quantified and will be discussed. Results from the microstructure based 3D simulations were found to be in good agreement with the experimental observations, indicating the importance and effectiveness of 3D microstructure-based simulations.

4:30 PM
A Formulation Based on Fast Fourier Transforms for the Calculation of the Micromechanical Behavior of Plastically Deformed 3-D Polycrystals: *Ricardo A. Lebensohn*[1]; [1]Los Alamos National Laboratory

In this work we present a numerical formulation based on Fast Fourier Transforms to efficiently obtain the micromechanical fields in plastically deformed 3-D polycrystals. This formulation was developed in the last decade by P.Suquet and coworkers as a fast algorithm to compute the elastic and elastoplastic response of composites, using as input a digital image of their microstructures. The model provides an exact solution of the governing equations and has better performance than a Finite Element calculation for the same purpose and resolution. This formulation has been in turn adapted to deal with 3-D polycrystals deforming by dislocation glide (R.Lebensohn, Acta Mater. 49, 2723, 2001). To illustrate its capabilities we will show results for a periodic polycrystal generated by Voronoi tessellation. The constituent grains are strongly anisotropic ice crystals. The results show transgranular deformation bands, stress concentrations near triple junctions and non-basal activity in unfavorably oriented grains.

4:50 PM
Modeling Deformation and Fracture Phenomena in 3 Dimensions: *Diana Farkas*[1]; [1]Virginia Tech

This work analyzes the 3 dimensional aspects of phenomena observed in plastic deformation of polycrystalline metallic materials at the nano scale. The studies are based on molecular dynamics simulations of deformation and fracture response in these materials. We specifically point out the limitations of modeling these phenomena in a quasi 2 dimensional framework. We also discuss techniques for visualization of the results of the 3D simulations, including sectioning and CAVE virtual reality visualization.

5:10 PM
Three-Dimensional Phase-Field Simulations of Equilibrium Morphology of Misfitting Precipitates: *Jingxian Zhang*[1]; Weiming Feng[1]; Shenyang Hu[2]; Zi-Kui Liu[1]; Long-Qing Chen[1]; [1]Pennsylvania State University; [2]Los Alamos National Laboratory

Elastic energy arising from a difference of lattice parameter between precipitate and parent phases have a strong influence on the equilibrium morphology of the precipitates. It depends on many parameters, including (i) elastic anisotropy, (ii) elastic inhomogeneity (the difference in the elastic constants of the two phases), and (iii) misfit strain. Recent advances in microelasticity theory and numerical simulations have made it possible to efficiently calculate the elastic energy for systems with rather general elastic anisotropies for the precipitate and matrix, arbitrarily large elastic inhomogeneity, and a general misfit strain. In this presentation, we studied the three-dimensional equilibrium shapes of misfitting precipitates by phase-field simulations. The effects of elastic constants, elastic inhomogeneity and misfit strains are investigated systematically. Relevant examples in real alloy systems will be discussed.

5:30 PM Invited
Interfacing Finite Element Simulations with Three-Dimensional Characterizations of Polycrystalline Microstructures: *Paul Dawson*[1]; [1]Cornell University

Experimental methods to characterize the microstructural state of polycrystalline samples have progressed rapidly in recent years. Automated serial sectioning combined with diffraction measurements provide digital images of the crystalline microstructure of material samples in three-dimensions. These complement x-ray tomography and bulk diffraction measurements to give both detailed definition of specific samples and statistically-based distributions of microstructural attributes. From a modeling perspective, the availability of spatially-resolved microstructures of actual samples together with measures of the likely variability of these microstructures offers fresh opportunities for investigating the links between microstructural state and mechanical properties, including how the state evolves under thermomechanical processing. In this presentation, we will discuss strategies for building virtual samples using mathematical representations of the material founded on the experimental characterization. Some samples are intended to closely replicate the experimental images, while others are intended for exploring variations that are consistent with the statistics of larger samples. The virtual samples evolve under loading via finite element simulations and the results are used to explore the connections between microstructural state and mechanical performance. This effort will be described in the context of a larger, ONR/DARPA-funded project that encompasses several thrusts to characterize and evolve polycrystalline microstructures in three-dimensions.

7th Global Innovations Symposium: Trends in Materials R&D for Sensor Manufacturing Technologies: Session I

Sponsored by: The Minerals, Metals and Materials Society, TMS Materials Processing and Manufacturing Division, TMS: Global Innovations Committee
Program Organizers: Hamish L. Fraser, Ohio State University; Iver E. Anderson, Iowa State University; John E. Smugeresky, Sandia National Laboratories

Monday PM — Room: 204A
March 13, 2006 — Location: Henry B. Gonzalez Convention Ctr.

Session Chair: Hamish L. Fraser, Ohio State University

2:00 PM Introductory Comments by John E. Smugeresky

2:05 PM Invited
Sensing: From Nanometers to Megameters: *Alton D. Romig*[1]; [1]Sandia National Laboratories

The application of advanced scientific, technological and engineering capabilities are essential to help our nation detect, repel, defeat, or mitigate the threat of chemical, biological, radiological, nuclear and explosive (CBRNE) weapons. Nanotechnology is a very promising area that will enable the creation of functional materials, devices, and systems by controlling matter at the atomic and molecular scales. Similarly, microtechnologies have helped produce smaller, smarter, and less costly sensors which feature desirable characteristics including lower power consumption, greater sensitivity, and better specificity than previous macro-level equivalents. Sensing systems based upon the integration of these technologies support a broad range of sensing applications – from the nm to Mm.

2:35 PM Invited
Global Innovations in Sensor Technologies: Materials Issues in Sensors for Automotive Applications: *Paul C. Killgoar*[1]; [1]Ford Motor Company

The number and variety of sensors used in automobiles has dramatically increased over the past several decades, a trend that is expected to continue in the future. Sensors are used in four major areas: active and passive safety systems, powertrain control systems, emissions control and monitoring systems, and climate control systems. Automotive safety technologies have evolved from seat belts and single-stage air bags to individually tailorable occupant protection systems in part because of affordable, sensitive accelerometers and occupant sensors. Increasingly refined interactive vehicle dynamics systems are enabled by body height, yaw, and other sensors. The availability of diverse physical and chemical sensors capable of operating in the harsh automotive environment, together with improvements in engine and catalyst technologies, has enabled far more precise and effective control of engine performance and emissions than in the past. The continuous improvements and new directions in safety, powertrain (gasoline, clean diesel, electric hybrid, hydrogen), emissions, and climate control require new and improved sensors. The principles and limitations of various automotive sensors and some of the evolving needs will be described. A number of new sensors are close to being production-ready, while others are still very much in the research and development stage. In this presentation, particular emphasis will be placed on the materials challenges, because cost and durabilityrequirements severely constrain the possible automotive sensor and materials solutions.

3:05 PM Invited
Materials Which Undergo a First Order Transition as Sensors – $Gd_5(Si_xGe_{1-x})_4$: *Karl A. Gschneidner*[1]; Min Zou[1]; H. Tang[1]; Vitalij K. Pecharsky[1]; [1]Iowa State University

$Gd_5(Si_xGe_{1-x})_4$ undergoes a magnetostructural first order transition between 40 and 275K, depending upon the Si to Ge ratio (high Si – high temperature). When the $Gd_5(Si_xGe_{1-x})_4$ transforms, it spontaneously generates a voltage (SGV). The SGV can be utilized in sensors, which respond not only to changes in temperature, pressure, and/or magnetic field,

but most importantly to the rates of their changes without the need for a complicated analysis of signals. Furthermore, all of this can be done by a single sensor requiring no standby power.

3:35 PM Break

3:50 PM Invited
Nanostructured Materials for Infrared Detection: *Gail J. Brown*[1]; [1]Air Force Research Laboratory

Quantum Confinement effects in semiconductor heterostructures has opened up many new approaches to designing infrared sensing materials. These nanostructured heterostructures come in a variety of forms such as quantum wells, quantum wires, quantum dots and superlattices. In addition, carbon nanotubes, colloidal nanoparticles and photonic crystals are attracting some interest for infrared detector applications. An attractive feature of all these materials is the ability to tailor the optical and electrical properties by changing simple parameters like layer thickness, materials composition, and layer combinations. Depending on the materials used, the nanoscale heterostructures can be designed for optical absorption anywhere from the ultraviolet to terahertz portion of the electromagnetic spectrum. This talk is an overview of these various materials and how they may be applied to infrared sensing.

4:20 PM Invited
Development and Application of Gas Sensing Technologies for Combustion Processes: *Prabir K. Dutta*[1]; [1]Ohio State University

The Center for Industrial Sensors and Measurements at The Ohio State University is developing microsensors to monitor combustion processes. Our approach in designing highly selective sensors includes optimized sensing principles, novel materials and use of catalysts. For O2 sensing, potentiometric measurements with internal references and a novel sealing technology is being developed. A potentiometric design with a catalyst filter is the basis for a total NOx sensor. CO sensing is being done with titania, modified by catalysts to produce selectivity. Hydrocarbon sensing exploits a filter that oxidizes the hydrocarbon to water. The CO2 sensor is based on a Li-conducting electrolyte. Miniaturized versions of these sensors are being integrated into a sensor array with data analysis by non linear regression techniques. A complete combustion monitoring/optimization system is possible for the first time with the miniaturized sensor arrays and is expected to lead to significant energy savings as well as minimizing emissions.

4:50 PM Invited
Issues Regarding Present and Future Characterization of Nanomaterials for Sensors at the Atomic Scale: *David B. Williams*[1]; [1]Lehigh University

In the main, the scale of sensor devices has been decreasing significantly during the development of nanomaterials. The processes that govern these sensors occur generally on the nanometer, or smaller, scale, and so it is important to have techniques for characterization at the atomic scale. This includes morphological information as well as compositional and chemical information obtained from spectral analysis. In this paper, the techniques available presently for such characterization will be described and limitations to resolution outlined. In concert with dramatic and revolutionary advances that have been made in the very recent past regarding aberration-corrected electron microscopy, solutions to presnt-day limitations will be described. Exciting examples of the application of these new instruments to nanomaterials for sensor applications will be presented. These will include spatial resolution imaging close to 0.06nm and spectral analyses, similar to those obtained by EXAFS, from regions defined by incident beam diameters of ˜1nm.

A Century of Nickel Alloy Discovery and Innovation: Session I

Sponsored by: The Minerals, Metals and Materials Society, TMS Structural Materials Division, TMS: High Temperature Alloys Committee
Program Organizers: Lewis Edward Shoemaker, Special Metals Corporation; Gaylord Smith, Special Metals Corporation

Monday PM — Room: 209
March 13, 2006 — Location: Henry B. Gonzalez Convention Ctr.

Session Chair: Lewis Edward Shoemaker, Special Metals Corporation

2:00 PM Invited
A Century of Discoveries, Inventors and New Nickel Alloys: *Shailesh Jayanti Patel*[1]; [1]Special Metals Corporation

The 20th century was an explosive period for the growth of the nickel industry beginning in 1906 with the development of Monel metal. What followed over the next 100 years is literally hundreds of new alloys uniquely designed for a multitude of industries in scores of applications. Leading the charge was the International Nickel Company with major new alloys in every decade. This impressive track record is briefly reviewed and acknowledgement given to a number of the prolific inventors that pioneered new fields of alloy development. Acknowledgement is equally given to the major metallurgical discoveries made by the metallurgists of the International Nickel Company, including gamma prime hardening of nickel alloys, ductilization of cast iron, the role of nickel in inhibiting stress corrosion cracking, maraging, mechanical alloying and the Pilling/Bedworth ratio of scale adhesion.

2:20 PM Invited
A Century of Monel Metal 1906 - 2006: *Lewis Edward Shoemaker*[1]; Gaylord D. Smith[1]; [1]Special Metals Corporation

Monel can arguably be considered the first nickel-base, corrosion-resistant alloy developed. It is essentially a binary alloy of nickel and copper. Since its ratio of nickel to copper is the same as that found in the ore from which it is derived, it can also be considered a “natural” alloy. Being patented in 1906, Monel is ready to celebrate its 100th birthday. Over its first century it has seen use in many different applications in many different industries ranging from huge naval leviathans to tiny electronic components and from food processing to gasoline production to electric power generation. The alloy and its descendants continue to be widely used today and it seems likely that trend will continue into the next century and beyond.

2:40 PM Invited
The Evolution of Solid Solution Nickel-Base Alloys for Corrosion Applications: *Galen Hodge*[1]; [1]Materials Technology Institute

The element nickel has some interesting metallurgical and electrochemical properties that make it an important material in the chemical industry. One of those is its ability to dissolve and hold in solid solution significant amounts of other alloying elements. This ability has made it possible to develop a large number of solid solution single-phase corrosion resistant alloys. Alloys containing iron, chromium, molybdenum and tungsten have, therefore, been developed to support more aggressive applications in the chemical industry. This paper will review the development of several of these alloys, describe their properties and applications.

3:00 PM Invited
The Evolution of Cast Nickel-Base Superalloys: *Tresa M. Pollock*[1]; [1]University of Michigan

Investment casting of complex nickel base superalloys has enabled continuous increases in their properties and performance of cast components in a wide range of applications, and particularly in gas turbine engines. Processing advances that permit a high degree of control of cast microstructure will be reviewed. The complementary role of solidification modeling will be discussed. An overview of the evolution of the chemistry of cast alloys will be presented. Finally, recent developments in single crystal growth will be highlighted.

3:20 PM Invited
Evolution of Wrought Age-Hardenable Superalloys: *Raymond F. Decker*[1]; [1]Thixomat

The discovery of gamma prime hardening early in the 20th century seeded a continuous evolution of remarkable engineering alloys, the Superalloys. This high technology field grows even to this day, some 85 years later. The sequence of development of all the wrought Superalloys will be traced as part of the story of the enlightenment gained on alloy theory and hardening mechanisms. Skillful use of the latest in composition/property theory has been the hallmark of Superalloy developments. Revolutionary processing discoveries have played their role. Finally, these alloys have enjoyed an eager market pull in ever evolving high tech applications.

3:40 PM Break

4:00 PM Panel Discussion
Future Trends in the Key Markets Served by Nickel Alloys: A brief introduction of the current status and future of materials technology in each industry followed the opportunity for audience comments, questions, and open discussion.

Aerospace Industry

Power Industry

Oil, Gas and Petrochemical Industry

Nickel Alloy Trends in China

Advanced Materials for Energy Conversion III: A Symposium in Honor of Drs. Gary Sandrock, Louis Schlapbach, and Seijirau Suda: FreedomCAR and Fuel Partnership-Metal Hydrides I

Sponsored by: The Minerals, Metals and Materials Society, TMS Light Metals Division, TMS: Reactive Metals Committee
Program Organizers: Dhanesh Chandra, University of Nevada; John J. Petrovic, Petrovic and Associates; Renato G. Bautista, University of Nevada; M. Ashraf Imam, Naval Research Laboratory

Monday PM — Room: 214B
March 13, 2006 — Location: Henry B. Gonzalez Convention Ctr.

Session Chairs: Scott Jorgensen, General Motors; Farshad Bavarian, Chevron Texaco Technology Ventures LLC; Sunita Satyapal, U.S. Department of Energy

2:00 PM Plenary
Overview of DOE Metal Hydride Center of Excellence: *James C. Wang*[1]; Jay Keller[1]; [1]Sandia National Laboratories

In July 2003, The Office of Hydrogen, Fuel Cells and Infrastructure Technologies of the Department of Energy (DOE) Office of Energy Efficiency and Renewable Energy solicited Grand Challenge Proposals to establish three Centers of Excellence in hydrogen storage developments for reversible metal hydrides, non-reversible chemical hydrides and carbon storage materials, respectively. The program mission is to research and develop cost-effective, on-board hydrogen storage systems that enable a minimum range of 300 miles within the weight and volume constraints of the vehicle. Currently, no hydrogen storage technology available can meet the DOE cost and performance targets. In April 2004, Sandia National Laboratories was selected by DOE to lead the Metal Hydride Center of Excellence with partners from 5 other national laboratories. We will present the organization and recent accomplishments of the Metal Hydride Center which is confident to accomplish DOE/FreedomCAR objectives for 2010 in hydrogen storage for vehicular transportation applications.

2:25 PM Plenary
A Thermodynamic Database for Metal-Hydrogen Systems: *Ursula R. Kattner*[1]; [1]National Institute of Standards and Technology

The thermodynamic properties of metal-hydrogen systems are key to assessing the suitability of particular systems for hydrogen storage. Thermodynamic modeling using the Calphad method provides a way to incorporate results from experimental investigations and ab-initio calculations into an overall temperature-pressure-composition framework. The calculations provide temperature and pressure of the hydriding reaction as well as heats of reaction and reaction sequences. A comprehensive thermodynamic database with Gibbs energy functions for the phases in metal-hydrogen systems and relevant metal-metal systems has been assembled from published data evaluations and newly generated thermodynamic descriptions. The initial focus in the construction of the database is on ternary and quaternary hydride systems with light elements.

2:50 PM Plenary
Novel Complex Hydrides for Hydrogen Storage: *Ragaiy Zidan*[1]; [1]Savannah River National Laboratory

The aim of the overall effort is to produce hydrogen storage materials of high hydrogen capacity higher than 8% by weight, stable with cycling and possessing favorable thermodynamics and kinetics characteristics compatible with on-board hydrogen storage transportation applications. In order to achieve this goal new methods for material synthesis are employed and guided by theoretical modeling, thermodynamic and material structural characterization. A new material synthesis method, molten state process, was developed and tested. This method is used to modify and form new complex hydride compounds with the desired characteristics. Other possible high capacity hydrides are also investigated.

3:10 PM Keynote
An Overview of Analytical Techniques Being Used to Characterize Today's Most Advanced Hydrogen Storage Materials: *Karl J. Gross*[1]; [1]Sandia National Laboratories

The wide variety of materials being proposed for hydrogen storage today present a number of different challenges to the researcher from an analytical characterization perspective. These include both evaluating the true performance of the materials for real-world applications as well as understanding the underlying physical mechanisms controlling the materials properties. An overview will be presented on the state of the art analytical methods for characterizing the hydrogen storage properties of materials. Some challenges to measurements on particular types of materials or conditions and in will be discussed.

3:30 PM Invited
Neutron and Synchrotron Studies on Li-Based Nitride and Hydride: *Wen-Ming Chien*[1]; Dhanesh Chandra[1]; Ashfia Huq[2]; James W. Richardson, Jr.[2]; Evan Maxey[2]; Martin Kunz[3]; Sirine Fakra[3]; [1]University of Nevada-Reno; [2]Argonne National Laboratory; [3]Lawrence Berkeley National Laboratory

Thermal expansions and phase identification of Li3N and LiAlD4 samples have been studied by using time-of-flight (TOF) neutron powder diffraction (NPD) and synchrotron diffraction methods. Low temperature neutron powder diffraction studies have been performed for both Li3N and LiAlD4 samples from 10 K to 300 K. Neutron and synchrotron studies of Li3N show that commercial Li3N is a two phase mixture (β+β). It was shown ~70 wt.% α-Li3N and ~30 wt.% β-Li3N for the commercial Li3N. Crystal structures of both α and β phases of Li3N are hexagonal, and LiAlD4 is monoclinic. Volume expansions of Li3N α+β phases are 0.56% and 1.1%, respectively, and for LiAlD4 is 0.88% form 10 K to 300 K. Detail lattice and volume expansions will be presented.

3:50 PM Break

4:05 PM Invited
Theoretical Contributions towards the Development of Storage Media and Related Materials for Hydrogen Processing: *Susanne Marie Opalka*[1]; Donald Anton[1]; Thomas Vanderspurt[1]; [1]United Technologies Research Center

Realization of the hydrogen economy will require new materials with unprecedented performance attributes for hydrogen generation, storage, and delivery. To meet these challenges, recent advances in first-principles methodologies are currently being used to guide and streamline the experimental development of materials, such as hydrogen storage media, fuel processing catalysts, and hydrogen-selective membranes. Implemen-

tation of these methodologies has been focused along two fronts: first, coupling of theoretical methodologies for enhanced physical property prediction, and second, the integration of modeling as an investigative tool alongside experimentation. The atomic-thermodynamic methodologies used to survey broad compositional phase space for hydrogen storage media with enhanced retrievable capacity will be discussed in detail, with special emphasis on the approaches used to create new candidate phase structures for evaluation. Additional examples will be used to highlight the unique role that theoretical methodologies play in elucidating mechanisms, and guiding the experimental optimization of hydrogen storage media.

4:25 PM Invited

Aluminum Hydride (AlH3) as a Hydrogen Storage Compound: *Jason Greatz*[1]; James J. Reilly[1]; Gary Sandrock[2]; John Johnson[1]; Wei Min Zhou[1]; James Wegrzyn[1]; [1]Brookhaven National Laboratory; [2]Brookhaven National Laboratory/Sandia National Laboratory

AlH3 is a covalent hydride known for more than 60 years. It is a very attractive medium for on-board automotive hydrogen storage since it contains 10.1 wt.% hydrogen with a density of 1.48 g/ml. There are 7 non-solvated AlH3 phases, α, α', β, γ, δ, ε, ζ. The properties of α-AlH3 obtained from the Dow Chemical company in 1980 has been previously reported. Here we present a description of the thermodynamic and kinetic properties of freshly prepared α, β and γ AlH3. In all cases the decomposition kinetics are below 100 degrees C and will meet DOE 2010 gravimetric and volumetric vehicular system targets (6 wt% H2 and 0.045 kg/l). However further research is needed to develop a practical regeneration process for the dehydrided material.

4:45 PM Keynote

Risk Assessment of High Capacity Solid State Hydrides: *Donald L. Anton*[1]; Frank E. Lynch[2]; Joseph Senecal[3]; [1]United Technologies; [2]Hydrogen Components, Inc.; [3]Kidde-Fenwal, Inc.

A critical consideration in the design of commercial hydrogen storage systems is safe operation. In the search for high hydrogen capacity materials such as alanates, this attribute has been overlooked. Conventional metal hydrides have been documented to be relatively safe, and this has fallaciously led to confidence in all hydrides. While the US Dept. of Transportation has detailed guidelines for the determination of risks associated with the transport of hazardous chemicals, no guideline exist for comparing the relative safety of new hydride materials. This study was instituted to define tests appropriate for determining the risks associated with using complex hydrides and to apply these tests to catalyzed $NaAlH_4$. Standardized ASTM and UN-DOT tests were identified. These tests and results for 2%$TiCl_3$ catalyzed $NaAlH_4$ will be described. The risks in handling and using these materials will be summarized and experiences gained in synthesizing 30 kg of catalyzed $NaAlH_4$ reviewed.

5:05 PM

First Principles Calculations of Destabilized Alloys for Hydrogen Storage Applications: *Sudhakar V. Alapati*[1]; Bing Dai[2]; Karl Johnson[2]; David S. Sholl[1]; [1]Carnegie Mellon University; [2]University of Pittsburgh

A novel approach to hydrogen storage has been proposed recently that utilizes destabilization of metal hydrides with other materials. The hydrides of period 2 and 3 metals have relatively high hydrogen densities but are thermodynamically very stable, releasing hydrogen only at high temperatures. Vajo et al. have shown that the thermodynamics of the reaction can be modified by using additives to form compounds in the dehydrogenated state that are stable with respect to the constituents of the initial reaction. Having a stabilized dehydrogenated state reduces the enthalpy of dehydrogenation and increases the equilibrium partial pressure of the dehydrogenation reaction. We have calculated enthalpies for destabilization reactions from density functional theory. Comparison with experiments show very good agreement for known reactions. We have predicted heats of reactions for a large number of hypothetical reactions and have identified promising candidates. We discuss calculation of dissociation pressures and kinetics.

Alumina and Bauxite: Solids/Liquid Separation

Sponsored by: The Minerals, Metals and Materials Society, TMS Light Metals Division, TMS: Aluminum Committee
Program Organizers: Jean Doucet, Alcan Inc; Dag Olsen, Hydro Aluminium Primary Metals; Travis J. Galloway, Century Aluminum Company

Monday PM Room: 7B
March 13, 2006 Location: Henry B. Gonzalez Convention Ctr.

Session Chair: Monique Authier, Alcan Inc

2:00 PM Introductory Comments

2:10 PM

Development of New Polyacrylate Flocculants for Red Mud Clarification: *Kevin L. O'Brien*[1]; Everett C. Phillips[1]; [1]Nalco Company

Conventional polyacrylate flocculants have been widely used to settle red mud in the Bayer process over the past two decades. A new manufacturing process has led to the development of higher molecular weight polyacrylate flocculants that outperform existing polyacrylate flocculants by 20% or more. Commercialization of the new polyacrylate flocculants has allowed plants to reduce overall consumption of flocculant. Lab test results and plant applications of these new flocculants at several refineries are summarized in this paper. Other benefits of these new flocculants such as their impact on mud rheological properties are currently under investigation and will also be discussed.

2:35 PM

Effect of Flocculant Molecular Weight on Rheology: *Donald P. Spitzer*[1]; Qi Dai[1]; [1]Cytec Industries Inc

Any polymeric flocculant used to settle suspended mud solids in reasonable times increases underflow mud yield stress, making the mud more difficult to flow. Yield stress (at a given solids concentration) always increases with polymer dosage, but depends somewhat on the type of polymer used. Primary emphasis of this paper is on the effects of molecular weight and the finding that, over quite a wide range, rheology does not depend on molecular weight. Thus, for lowest possible yield stress, molecular weight should be as high as possible, since this will give the lowest dosage for the required settling rate.

3:00 PM

A Fractal Model Describing the Aggregation of Various Mineral Materials: *Michel J. Gagnon*[1]; André Leclerc[1]; Guy Simard[1]; René Verreault[1]; Guy Péloquin[1]; [1]Université du Québec à Chicoutimi

The agglomeration of the particulate materials is necessary in many mineral processes. Depending upon physical and chemical parameters, the aggregates generated demonstrate specific density-size distributions that reflect the dominant agglomeration process. A fractal and empirical model was initially constructed to describe the red mud flocculation using simple variables such as density, particle sizes and fractal order. The application of the model to other data sets found in the scientific literature demonstrates a wider utilization of the model and was helpful in the development of a criterion that should facilitate the identification of the dominant mechanism by which the aggregation occurs. In this paper, data from different sources, various mineral materials and agglomeration processes is analysed and compared in the light of the proposed model and criterion. The values obtained with the linear fit are discussed in relation with the coagulation or flocculation, the fractal dimension and the resulting fractal structures.

3:25 PM

Study on the Clarification of a Red Mud Slurry during Flocculation: *Mélanie Normandin*[1]; Michel Gagnon[1]; Guy Simard[1]; André Leclerc[1]; René Verreault[1]; Guy Péloquin[2]; [1]Université du Québec à Chicoutimi; [2]Centre de Recherche et de Développement Arvida

One of the important steps in the Bayer process is the solid-liquid separation by which the particulate materials are removed from the feed slurry. Obtaining perfect overflow clarity is one of the ultimate goals of the alumina industry. In this study, the parameters that can influence the clarity

of the overflow liquor resulting from the flocculation of the red mud slurry are systematically evaluated. Several laboratory tests are done combining commercial synthetic flocculants and new polymers. By varying the concentration of polymer solutions, the quantity and the sequence of introduction of polymeric materials, extremely low levels of turbidity were found in the overflow liquor. This represents a definite step toward the objective of reaching the absolute decantation by which perfectly clear overflow liquor is obtained right out of the decanters.

3:50 PM Break

4:10 PM

Waste Water Treatment Methods: *Dana Smith*[1]; Fred S. Williams[2]; Scott Moffatt[3]; [1]Alcoa; [2]CMIS Corporation; [3]Cytec Industries Inc

Alcoa's Point Comfort, Texas industrial facility is a combination of a bauxite refining plant utilizing the Bayer process and an aluminum fluoride production plant. Due to the location's use of dry stack technology for disposing of the bauxite residue, the pond surface areas for evaporation are minimal compared to the rainfall catchment areas. This results in the periodic need to reduce accumulated volumes of storm water at the Residue Disposal Area (RDA). Described in this paper will be options for treating a combination of waste waters from the RDA. The current water treatment method utilizes ferric sulfate for total organic carbon (TOC) and metallic ion adsorption. The precipitated solids are separated and the treated water neutralized prior to discharge. Experimental work will also be presented for the treatment of Bayer process water alone.

Aluminum Reduction Technology: Cell Development and Operations - Part I

Sponsored by: The Minerals, Metals and Materials Society, TMS Light Metals Division, TMS: Aluminum Committee
Program Organizers: Stephen Joseph Lindsay, Alcoa Inc; Tor Bjarne Pedersen, Elkem Aluminium ANS; Travis J. Galloway, Century Aluminum Company

Monday PM — Room: 7A
March 13, 2006 — Location: Henry B. Gonzalez Convention Ctr.

Session Chair: Mark Taylor, University of Auckland

2:00 PM

Alouette Line 2: Starting-Up the Right Way: *Pierre Reny*[1]; Joe H. Lombard[1]; [1]Aluminerie Alouette Inc

Alouette Aluminum Smelter, located in Sept-Iles, Quebec, Canada successfully started its 330 AP30 pots expansion during the first months of 2005. Evidently, a plethora of challenges faced both the construction and operation teams at all steps of the project. This article focuses on one of the broader challenges that was at the root of many others, namely to maintain and improve the performance of the existing part of the smelter while so much attention is devoted to the project start-up of the new line. This article will describe how innovative project organization, along with well planned operational changes implementation allowed to smoothly start the anode plant, reduction and casthouse expansions while improving productivity of the older part of the smelter. Other critical aspects such as emissions control, safety and work quality during start-up as well as interaction with the project are discussed.

2:25 PM

35 Years of Improvement at Anglesey Aluminium: *Daniel Woodfield*[1]; Dewi Roberts[1]; Mike Wilson[1]; Gerry Forde[1]; [1]Anglesey Aluminium Metal

As part of our 35th anniversary year, this paper reviews 35 years of technical improvement at Anglesey Aluminium, focusing on improvements in hot metal production. From a low of 76 000 t in 1973, hot metal production has almost doubled to today's levels of 147, 000 tpa. Amperage has increased from 134 kA to 172 kA and CE% from the mid 80's to 95%. Key aspects of achieving these outcomes in a cost effective manner are discussed, in particular changes to the anode and anode assembly and improvements in feed control.

2:50 PM

Reduction of Amperage at New Zealand Aluminium Smelters: *Daniel Whitfield*[1]; Gabe Oldenhof[1]; [1]New Zealand Aluminium Smelters Ltd.

During 2004, the amperage of Line 3 at New Zealand Aluminium Smelters Ltd. had to be reduced to allow the line to run on only three out of four rectiformers, to allow maintenance to be performed on each of the four rectiformers. This paper details the reduction of amperage of Line 3 to 175kA (from 184.3kA) and the subsequent ramp up to 185 kA, and reports on various observations during this period. Despite the many changes during this possibly tumultuous period of operation, the line managed to make record current efficiency, power efficiency, and purity.Process knowledge gained from the amperage reduction period was used to develop the application for capital expenditure for a booster rectiformer connection, and avoid the need to repeat the exercise in the future.

3:15 PM

180 kA Booster Cells Operation at ALBRAS: *Jose Eduardo M. Blasques*[1]; Guilherme Epifano da Mota[1]; Handerson Penna Dias[1]; Giancarlo De Gregoriis[1]; [1]Aluminio Brasileiro ALBRAS S.A.

In recent years, Albras has been increasing line current. The necessary adjustments to the work practices and process variables need to be made on all potlines, which in this case means on 960 cells at the same time. It was a challenging task to adjust the operation to the new amperage. In July 2003 potlines II, III and IV were running at 173 kA and the goal at that time was to reach 180 kA. Preliminary trials were performed on a group of 10 boosted cells in order to investigate possible operational problems. It was decided to increase the amperage in three steps accompanied by continual evaluation of the state of the process. In July 2004 the target of 180 kA was achieved with good operational results. This paper presents the overall results, the parameter adjustments made during the amperage increase and how it was implemented on the other potlines.

3:40 PM

The Next Step to the AP3X-HALE Technology: Higher Amperage, Lower Energy and Economical Performances: *Oliver Martin*[1]; Claude Richard; [1]Alcan

The Aluminium Pechiney AP35 technology is presently the spearhead of the ALCAN technological offer. To maintain its technological leadership, Alcan has continued to optimise the AP35 and will soon propose to its clients an AP36 at 360kA. At the same time, an intensive technology development program aiming at continuing the amperage increase potential while improving the energy performance is started and should give rise to an AP37 in the next months. This article describes the operational tests allowing to bring the AP35 at a 360 kA level as well as the results to date of the R&D AP37 program (370 kA). The positioning of this technology is compared to, in technical and economical terms, the AP35 cell and shows advantageous benefits resulting in the investment and operation cost reduction program for future projects using ALCAN AP3X-HALE technologies.

4:05 PM

Development of the B32 Cell Technology: *David Billinghurst*[1]; Bill Paul[1]; Geoff Bearne[1]; Ian Coad[2]; [1]Comalco Research & Technical Support; [2]Boyne Smelters Ltd

In 2002 five prototype B32 cells were started at the Boyne Island Smelter (BSL) in Queensland, Australia. The purpose of this trial was to provide a magnetically compensated technology for use in an expansion of BSL Line 1 and 2. This required the development of a highly asymmetric busbar design capable of operating at a bay to bay spacing of 24 m. The cells were designed to operate at 265 kA, but were commissioned at 270 kA and are now running at 280 kA. The technology has achieved design targets and exceeded expectations. It is now considered suitable for expansion opportunities should they exist.

4:30 PM

Analysis of Prebake Anode Assembly of Hall-Heroult Cells to Enhance Life of Conductor Bar: Bir Kapoor[1]; *S. C. Tandon*[2]; R. N. Prasad[2]; K. Kamaraj[3]; [1]Aditya Birla Management Corporation Ltd; [2]Hindalco Industries Ltd.; [3]Indian Institute of Technology

Significant efforts have been made over the years at Hindalco Smelter Renukoot to improve the efficiency of smelter operation by pushing the

design limit of various components. Enhancing the life of copper bar conductor, which holds the anode assembly, is one such example. These bars are exposed to static load of the anode assembly and severe thermal conditions and due to bath proximity. Failure of these bars was seen due to cracks after few cycles, thus preventing repeated use of these bars. The causes of failure have been analyzed by conducting a combination of thermo-mechanical modeling and micro-structural analysis. A simple finite element model with experimentally measured temperatures as boundary conditions has been used for thermal stress analysis. The creep deformation has been identified as the primary mechanism. The point of onset of creep can be attributed to micro-structural deficiencies and high temperature exposure of the bar.

4:55 PM

Upgrading Outdated Rectifier Control Systems with an AC 800PEC Digital Controller: *Ann K Roberts*[1]; Joseph Frisch[1]; [1]ABB

Every industrial rectifier system must meet at least four basic requirements. The system must provide continuous, reliable, adequate and safe DC power. The costs of the aging installed base of high-power rectifier systems are mounting with process industries paying dearly with unreliable equipment and extended downtimes for maintenance. These financial losses are dramatic because rectifiers provide the DC current supply to a host of critical process applications. Over years electrical performance of a plant deteriorates. Implementation of conventional maintenance procedures is not practical to improve the availability, safety, productivity and efficiency. Failures in old control components generally cause longer down times since these parts are not available, obsolete or need to be repaired. The following paper presents results of recent upgrades of rectifier control systems by replacing the original installed control systems with a digital controller; leading to increased plant availability, resulting in a significant increase of production.

5:20 PM

Analysis of the Start-Up of Q-350 Prebaked Aluminum Reduction Cell: *Zeng Shuiping*[1]; Li Jinhong[1]; Lan Tao[2]; Ding Lei[1]; [1]North China University of Technology; [2]Qingtongxia Aluminum Plant

Q-350 prebaked alumina reduction cell line is the largest one in china. Some of the cells were started April 2004 at Qingtongxia aluminum plant in west China without industrial experiment beforehand. For the lack of experience, the start-up process has met some problems. This paper introduced the method for preheating and start-up of the cells, showed some typical data which include the computer sampling data and manual measuring one using the Dassie system, which is a comprehensive system integrated many kinds of function, and was designed specially for the aluminum production management. It was found that the metal instability and the volt rising schedule were the main problems, and it was difficult to set the cell voltage to the required value and keep the cell stable at same time. With consideration of the cell design, the paper indicated the defauts of start-up process and some improvements for cell operation.

5:40 PM End

Amiya Mukherjee Symposium on Processing and Mechanical Response of Engineering Materials: NanoProcessing for NanoGrain Materials

Sponsored by: The Minerals, Metals and Materials Society, TMS Materials Processing and Manufacturing Division, TMS Structural Materials Division, TMS/ASM: Mechanical Behavior of Materials Committee, TMS: Shaping and Forming Committee

Program Organizers: Judy Schneider, Mississippi State University; Rajiv S. Mishra, University of Missouri; Yuntian T. Zhu, Los Alamos National Laboratory; Khaled B. Morsi, San Diego State University; Viola L. Acoff, University of Alabama; Eric M. Taleff, University of Texas; Thomas R. Bieler, Michigan State University

Monday PM — Room: 217C
March 13, 2006 — Location: Henry B. Gonzalez Convention Ctr.

Session Chairs: Eric M. Taleff, University of Texas; Nathan A. Mara, University of California

2:00 PM Invited

Encounter between an Ancient Steel and Modern Science: *Srinivasa Ranganathan*[1]; [1]Indian Institute of Science

Wootz steel as an advanced material dominated several landscapes: the geographic landscape spanning the continents of Asia, Europe and the Americas; the historic landscape stretching over two millennia as maps of nations were redrawn and kingdoms rose and fell; the literary landscape as celebrated in myths and legends, poetry and drama, movies and plays; the linguistic landscape of Sanskrit, Arabic, Urdu, Japanese, Tamil, Telugu and Kannada; the religious landscape of Hinduism, Buddhism, Zoroastrianism, Judaism, Islam and Christianity. The study of this ancient steel inspired European metallurgists to unravel the link among processing, structure, properties and performance. It is amazing that very similar properties can be achieved by an alternate route involving laminates in in the Japanese swords. Several metallurgical themes - microalloying, spheroidization, dendrites, microsegregation, superplasticity, composites and nanowires - will be explored to establish wootz steel as an exemplar of the Materials Hypertetrahedron.

2:20 PM Invited

Engineering Structure on a Nanoscale Level to Achieve Targeted Properties in Steels: *Daniel Branagan*[1]; [1]NanoSteel Company

Essential aspects of solidification will be presented showing how solid state transformations can be used to refine the microstructural scale in 'steels' to achieve phase sizes in the nanoscale regime. By changing the kinetics of solidification, high undercoolings can be achieved allowing either, complete avoidance of nucleation resulting in a metallic glass which can be subsequently devitrified, or the achievement of an extremely rapid nucleation rates in order to form nanocrystalline scale phases directly during solidification. The achievement of nanoscale microstructures should not be considered the end goal but instead represents an enabling ability to develop vastly improved properties which are not possible on conventional length scales. Three case examples will be presented detailing the challenges and successful approaches that have been used to engineer the nanostructure of steels to achieve high energy density/high intrinsic coercivity, high strength/hardness, and high tensile elongation/low temperature superplasticity.

2:40 PM

Manufacturing of Miniaturized MEMS Parts by ECAP: *Georg Raab*[1]; Nikolay Krasilnikov[2]; Ruslan Valiev[1]; Juri Estrin[3]; [1]Ufa State University of Aviation Technology; [2]Ulyanovsk State University; [3]Clausthal University of Technology

Miniaturized MEMS parts, with dimensions below 2 mm, are exposed to rather tough service conditions. With their superior properties, materials with ultrafine structure offer themselves for manufacturing such parts. A range of MEMS parts, including cogwheels, axles and casings, are axially symmetrical, and it is possible to produce them by equal channel angular pressing (ECAP), thus combining the forming operation with the development of a desired microstructure. In such a process, the small di-

mensions of the products put serious limitations on the dimension tolerances, tribological conditions, strength of the tooling, etc. Here we report the results of a first feasibility study on manufacturing an axially symmetric part, viz. a cog wheel 2 mm in diameter, from Cu and Ni. Experiments combined with 3D simulations of the ECAP process will be presented along with data on the character of plastic flow, strength and microstructure of the parts manufactured.

3:00 PM

Microstructural Evolution during ECAE Processing of Ti-6Al-4V: Byungin Jung[1]; *Shankar M. Sastry*[1]; Rabindra N. Mahapatra[2]; [1]Washington University; [2]U.S. Navy

Microstructural evolultion during ECAE processing at 600°C and subsequent annealing at 700-1000°C was studied in Ti-6Al-4V with Widmanstatten α+β and equiaxed α+β microstructures In specimens containing Widmanstatten α+β microstructure, ECAE processing resulted in break up of beta phase and formation of 200-300 nm sized sub grains in α phase. Upon annealing, spheroidization of fragmented β occurred along with recrystallization in α phase resulting in a fine-grained equiaxed α+β microstructure with 2-3 micrometer grains developed. The resulting grain size is determined by the size and spacing of the spheroidized β phase. Specimens with the initial equiaxed α+β developed a coarser (> 6 micrometer sized) equiaxed α+β microstructure.

3:20 PM Invited

Comparison of Rapid Solidification Results in Improved RE2(Fe, Co)14B Magnet Alloys Due to Heat Flow and Nucleation Effects (RE=Nd+Y+Dy): *Iver E. Anderson*[1]; Nicholas L. Buelow[1]; Wei Tang[1]; Yaqiao Wu[1]; Peter K. Sokolowski[1]; Kevin Dennis[1]; Matthew J. Kramer[1]; Bill McCallum[1]; [1]Iowa State University

New YDy-based RE2(Fe, Co)14B ribbons and spherical powders for high temperature bonded magnets have been developed by melt spinning (MS) and gas atomization (GA), respectively. Useful magnetic properties from ambient to above 200C were achieved by optimizing compositions and microstructure. Above 125C, (BH)max of optimized alloy ribbon is superior to commercial ribbon. MS wheel speeds of 10-16 m/s produced comparable solidification structures to fine GA (He gas) powders, allowing extensive alloy design with MS. Effects of TiC and Zr additions on promoting glass formation and nucleation of 2-14-1 phase in ribbon and powder microstructures were studied systematically by SEM, TEM, XRD, and DTA. Translation of MS microstructures to GA powders seems to require both additions. Oxidation resistance during fine powder processing and retention of high temperature magnetic properties in polymer-bonded magnets were improved by development of a fluoride surface (15-40nm) layer treatment. Support from DOE-EERE-FCVT through Ames Laboratory contract W-7405-ENG-82.

3:40 PM

Comparison between Shot Peening and Surface Nanocrystallization and Hardening (SNH) Processes: *Leon L. Shaw*[1]; Kun Dai[1]; [1]University of Connecticut

The surface nanocrystallization and hardening (SNH) is a relatively new process that has been developed to enhance fatigue and wear resistances. The SNH is similar to widely-used shot peening in the sense that both processes entail repeated impacts of the surface of a workpiece with spheres. The difference between them lies in the sizes of spheres and the impact velocities used. Such a difference results in dramatic changes in kinetic energies and thus thicknesses of the deformation layer and the nanograin surface layer. In this study, finite element modeling is performed to provide quantitative description of these differences. The results show that the kinetic energy in the SNH process is typically 180 times larger than that in shot peening, and the deformation layer in the SNH process is about 10 times thicker than that generated in shot peening. The implication of these differences on fatigue resistance has been examined.

4:00 PM Break

4:10 PM Invited

Self-Assembly Approach towards Nano-Ordered Structures in High Temperature Ceramics: *Julin Wan*[1]; Patrick Malenfant[1]; Seth T. Taylor[1]; Sergio M. Loureiro[1]; Mohan Manoharan[1]; [1]General Electric Global Research Center

In an effort to simulate nanoscale structure with long-range order in natural ceramic structures such as nacre, a new approach called templated synthesis of polymer-derived ceramics was explored to build nano-order in a Si-C-N system. Polymeric precursors that lead to the desired ceramic composition were self-assembled using block copolymers as structure-directing agents. In this presentation, we describe the basic block copolymer physics that governs the formation of self-assembly, and the interactions that enables using this assembly as a template to build nanoscale order in ceramic precursors. Microstructures ranging from classic lamellar to cylindrical to more complicated morphologies are described, and their evolution is shown to vary sensitively with precursor chemistry, loading and heat-treatment history. It will be shown that the ordered nanoscale structure created in the block copolymer/precursor hybrids can be preserved through the pyrolysis process, thereby leading to ordered nanostructures in the final ceramic.

4:30 PM Invited

SPS: A High Strain Rate Low Temperature Forming Tool for Ceramics: Dongtao Jiang[1]; Dustin M. Hulbert[1]; Joshua D. Kuntz[2]; *Amiya K. Mukherjee*[1]; [1]University of California; [2]Lawrence Livermore National Laboratory

Spark plasma sintering technique is being widely used to produce nanocrystalline materials in virtue of rapid sintering at relatively lower temperatures. In this investigation, it is demonstrated that the technique can also be used to achieve high strain rate superplasticity at low temperatue that is impossible by using conventional methods. Fully dense Al2O3-ZrO2-MgAl2O4 was superplastically formed into a complex shape in SPS furnace with a strain rate of 10-2 at a temperature as low as 1150°C. Furthermore, a powder compact can be directly shaped into complex shape by SPS technique, combining sintering and forming into one step. The product is fully dense and free of surface crack. It is argued that the SPS one-step forming is closely related to the superplastic behaviour that might be attributed to the enhanced diffusion under external electric field. Those results indicate that SPS can be a very competitive forming tool for ceramics.

4:50 PM

Development of a Nano-Scale Bioceramic: *Tien B. Tran*[1]; Vladimir Y. Kodash[1]; James F. Shackelford[1]; Joanna R. Groza[1]; [1]University of California

The use of hydroxyapatite (HA), a recognized biocompatible ceramic, is limited to non-load-bearing orthopaedic applications due to its poor fracture toughness. Nanocrystalline HA powders were consolidated via the Field Activated Sintering Technique (FAST) in order to restrain grain growth to the nanoscale regime, thereby enhancing mechanical properties and *in vivo* performance. The method applied pulsed electrical current to powders under a light pressure and produced encouraging results. A density of 97% theoretical was achieved at a relatively low temperature (850°C) in 1 minute under a pressure of 45 MPa. Scanning electron microscopy revealed a final microstructure consisting of nanosized grains. Mechanical properties and *in vitro* characterization of the resulting material will be reported in regards to its potential for load-bearing orthopaedic applications, such as a delivery system for bone morphogenetic proteins (BMP).

5:10 PM Invited

Processing/Microstructure/Property Relationships in Severely Deformed Tantalum: Suveen N. Mathaudhu[1]; *K. Ted Hartwig*[1]; [1]Texas A&M University

Bars of as-cast, large grained and highly textured Ta were deformed by multipass equal channel angular extrusion (ECAE) at room temperature to strains of 4.6 through 90º die-angle tooling. Comparisons of the microstructure and mechanical properties after four consecutive extrusions via route C (180º rotation between passes) Bc (90º rotation between passes) and E (2C, 90º rotation then 2C) are made in both the as-worked (submicron- scale grains) and recrystallized (micron-scale grains) conditions. Yield strength decreases from ~950 MPa in the as-worked ($\varepsilon = 4.6$) state to ~200 MPa in the recrystallized state, while the ductility (%EL) increases from ~10% to ~50%. Results show that the mechanical behavior of as-worked and recrystallized tantalum follows a typical Hall-Petch relationship. Empirical equations correlating the grain size, microhardness, yield

strength and tensile strength in heavily worked and recrystallized Ta are presented.

5:30 PM Invited
Interface Stability in Copper-Niobium Nanolayered Composites: *Amit Misra*[1]; Richard G. Hoagland[1]; [1]Los Alamos National Laboratory

Sputter deposited metallic nanolaminates exhibit ultra high hardness when the bilayer periods approach nanometer dimensions. In this presentation, we report on the morphological stability of interfaces in Cu-Nb nanolayered composites. The origins of the unusual thermal stability of the layered structure, at annealing conditions where layer pinch-off and spheroidization is expected but did not occur, is discussed. This research is aimed at exploring the elevated temperature properties of nanolayered composites and has involved collaborations with Prof. Mukherjee's group. In another set of experiments, Cu-Nb multilayers were implanted with Helium ions at room temperature prior to annealing. With decreasing layer thickness in the nanometer range, a suppression of bubble growth and subsequent blistering during annealing of radiated samples was observed. The relation of the interfaces to the evolution of radiation damage will be discussed. This research is funded by DOE, Office of Science, Office of Basic Energy Sciences and LANL LDRD.

5:50 PM
Ultrafine Grain-Sized Zirconium by Dynamic Deformation: *Bimal K. Kad*[1]; Marc A. Meyers[1]; Joerg-Martin Gebert[2]; Maria Teresa Perez-Prado[3]; Michael E. Kassner[4]; [1]University of California, San Diego; [2]University of Karlsruhe; [3]Centro Nacional de Investigaciones Metalúrgicas; [4]University of Southern California

Zirconium (gs: 14 um) was subjected to high plastic shear strain (25-100) at 104 s-1 in hat-shaped specimen/Hopkinson bar. Region of intense plastic deformation (10-25 μm thick) is produced which is analyzed by EBSD and TEM. Microstructure within shear band is characterized by equiaxed grains with size of 200 nm. Temperature, calculated with Zerilli-Armstrong equation, is 930 K for shear strain of 100. EBSD reveals a strong fiber texture. Ultrafine grain structure observed is similar to one obtained in SPD processes (ECAE/ECAP), suggesting that mechanism of grain refinement is same in spite of differences in strain rate and thermal excursion. Mechanism is proposed for breakup of existing equiaxed microstructure into ultra-fine structure: 1. formation of elongated cells and sub-grains; 2. increased misorientation between neighboring grains and breakup of elongated grains into smaller units; 3. rotation of boundaries by grain-boundary rotation and formation of equiaxed structure. Support: NSF DMR 0419222,CMS-0210173.

Biological Materials Science: Computational Biomaterials/The Biomaterials-Tissue Interface

Sponsored by: The Minerals, Metals and Materials Society, ASM International, TMS Structural Materials Division, TMS: Biomaterials Committee, TMS/ASM: Mechanical Behavior of Materials Committee
Program Organizers: Andrea M. Hodge, Lawrence Livermore National Laboratory; Chwee Teck Lim, National University of Singapore; Richard Alan LeSar, Los Alamos National Laboratory; Marc Andre Meyers, University of California, San Diego

Monday PM Room: 212A
March 13, 2006 Location: Henry B. Gonzalez Convention Ctr.

Session Chairs: Richard Alan LeSar, Los Alamos National Laboratory; Sungho Jin, University of California

2:00 PM Invited
Coarse-Grained Model of Biomolecular Structure and Dynamics: *Richard Alan LeSar*[1]; Antonio Redondo[1]; [1]Los Alamos National Laboratory

Direct modeling and simulation of large-scale biomolecular structures is a computational grand challenge owing to the extremely large numbers of atoms and the short time scales inherent in an atomistic description. We will describe a recently-developed coarse-grained simulation method designed to model the structure and dynamics of proteins and other large biomolecular structures. While being coarse-grained in nature, the method preserves the essential properties of the individual molecules and their interactions with each other and with solvent molecules. It is a calculationally-flexible method that enables us to include complex effects in a simplified, but accurate way. We will show applications of the method to both simple protein structures as well as larger-scale biomolecular structures, e.g., microtubules.

2:30 PM Invited
Molecular-Level Modeling for Erythrocyte Deformation: Ming Dao[1]; Ju Li[2]; *Subra Suresh*[1]; [1]Massachusetts Institute of Technology; [2]Ohio State University

The mechanical properties of erythrocytes (red blood cells) influence strongly their biological functions and the onset, progression and consequences of a number of human diseases. The hyperelasticity characteristics of erythrocyte subjected to finite-deformation stretching by laser tweezers is studied at the spectrin level by molecular dynamics and conjugate gradient energy minimization methods as well as at the continuum level by finite-element modeling. We have further developed an on-the-fly homogenization scheme for studying the mechanics of living cells that comprise 2D/3D molecular networks as structural bases—Molecular Potential Finite-Element Method (MPFEM). For the spectrin network that provides membrane shear elasticity, we use the worm-like chain (WLC) potential for single spectrin molecular response. MPFEM provides a bridge between whole-cell mechanics and single-molecule response as well as spectrin network structure. Connections among molecular structure, cell mechanical deformation and disease states related to *Plasmodium falciparum* malaria, heredity spherocytosis and Southeast Asian ovalocytosis are discussed.

3:00 PM
Modeling the Influence of Microstructure on Implantable Drug Delivery Devices: *James Aaron Warren*[1]; David M. Saylor[2]; [1]National Institute of Standards and Technology; [2]Food and Drug Administration

Experimental work has demonstrated that the microstructure of the polymer-drug mixture that coats a drug-eluting stent and other implantable devices can be extremely complex. From a materials science perspective, it is clear that this structure will influence the dissolution process, yet existing models are unable quantify the influence of this microstructure, or model the structures formation and its ensuing effects on dissolution. The address these issues we have developed a phase field model of the drug-polymer blend to allow realistic simulations of the fabrication ofdrug coated implantable devices. In addition to enabling the simulation of the microstructure formed during processing, the model properly accounts for the changing morphology and position of the drug-eluting boundary as the drug dissolves, as well as spinodal decomposition, dewetting, polycrystalline solidification and a host of other phenomena.

3:20 PM
Modeling Cell-Structure Evolution in Biological Multicellular Systems: Jose Munoz[1]; Kathy Barrett[2]; Buzz Baum[3]; *Mark Miodownik*[1]; [1]King's College London; [2]University College London; [3]Ludwig Institute for Cancer Research

In this work we use the finite element method to study the micromechanics and cell-structure evolution that occurs in biological multicellular systems. The phenomenon is analagous to microstructure evolution in metals, but with the fundamental difference that cells respond both passively and actively to forces. It is the active part that distinguishes the system as biological. These active forces have a big impact on the final structures and are most critical during organism growth when small changes can have a large phenotypic imapct. eg. spina bifida in Humans. We use FEM techniques to model cell mechanics in the presence of both active and passive forces during the early stages of embryo growth of flys (Drosophila). A novel master-slave approach is included to model the sliding process of the epithelium along the extracellular matrix.We show in the numerical results that the model can closely reproduce the invagination process and its mechanisms.

3:40 PM
Mechanisms of Cell Spreading on Porous Titanium Surfaces: *Winston O. Soboyejo*[1]; [1]Princeton University

This paper presents the mechanisms of cell spreading on porous Ti and Co-Cr surfaces with well controlled pore architectures and RGD surface

chemistries designed to promote increased adhesion. A combination of confocal and scanning electron microscopy is used to study how cells roll, adhere and spread on micron-scale and nano-scale surfaces. The mechanisms by which cells spread across porous gaps are also revealed. In selected cases, the cells spread over nano-particles and over each other until they bridge the gaps between the pores. The subsequent spreading and proliferation of cells then results in a configuration of cells/tissue that appears to be clamped to the porous structure. However, this is the integrated result of several processes that are elucidated by a combination of in-situ microscopy immuno-flourescence techniques, and x-ray computer tomography. The implications of the results are discussed for the design of porous architectures for osseo-integration.

4:00 PM Break

4:20 PM Invited
Enhanced Adhesion and Growth of Cells on Nanostructure Array: Brian Oh[1]; *Sungho Jin*[1]; [1]University of California

Nanostructures provide a very large surface area and topographical features suitable for cell adhesion and growth. Vertically aligned yet laterally spaced nanoscale TiO2 nanotubes have been grown on Ti by anodization, and the growth of MC3T3-E1 osteoblast cells and other types of cells on such nanotube array surface has been investigated. The adhesion/propagation of the cells is substantially improved by the topography of the TiO2 nanotubes with the filopodia of growing cells going into the nanotube pores, producing a locked-in cell structure. The presence of the nanotube structure induced a significant acceleration in the growth rate of osteoblast cells by as much as ~400%. The effect of various biological and materials parameters on cell growth will be described, and the design of desirable nanostructure for maximum cell growth kinetics and cell viability will be discussed.

4:50 PM
Hydroxyapatite Sol-Gel Coating on Titanium Alloys for Biomedical Applications: *Cui'e Wen*[1]; Wei Xu[2]; Wangyu Hu[2]; Meiheng Li[2]; [1]Deakin University; [2]Hunan University

Hydroxyapatite (HA) coating has many biological benefits such as direct bonding to bone and enhancement of new bone formation around it due to its chemical similarity with hard tissues. In the present study, a simple sol-gel method was developed for hydroxyapatite film deposition on titanium alloys for biomedical applications. Phase formation, surface morphology, and interfacial microstructure were investigated using DSC, XRD and SEM techniques. The hydroxyapatite film was spin-coated on the titanium alloy surface and then heat treated at difference temperatures. Results indicated that the HA phase begins to crystallize after a heat treatment at a relatively low temperature of 600°C; and the crystallinity increases with the increasing of the temperature. The HA film showed a porous structure and a thickness approximating 7 μm after certain heat treatment.

5:10 PM
Laser Textured Biomedical Surfaces for Cell/Surface Integration: *Winston Oluwole Soboyejo*[1]; [1]Princeton University

This paper presents the results of experimental studies of cell spreading and adhesion to laser textured Ti-6Al-4V surfaces. The surface textures associated with laser/materials interactions are elucidated via interferometry and scanning electron microscopy. Local changes in surface chemistry are then examined using energy dispersive x-ray spectroscopy before discussing the effects of microgroove geometry and chemistry on cell spreading on Ti-6Al-4V surfaces with/without RGD coatings. The adhesion between the cells and the textured/coated surface is quantified using shear assay and micro-pipette aspiration. The implications of the results are then discussed for the design of orthopedic/dental implants with improved adhesion to bone.

5:30 PM
Nanostructure, Dissolution and Morphology Characteristics of Novel Microcidal Silver Films Deposited by Magnetron Sputtering: *Sudhindra B. Sant*[1]; Kashmir S. Gill[2]; Robert E. Burrell[3]; [1]Twin Technologies Inc; [2]National Research Council of Canada; [3]University of Alberta

Novel microcidal silver films for burn dressings have been produced by magnetron sputtering. The nanostructure and dissolution characteristics of these films exhibiting antimicrobial behaviour were studied as a function of the process conditions, namely, gas composition, gas pressure and input power, using transmission electron microscopy (TEM), high-resolution scanning electron microscopy, X-ray photoelectron spectroscopy (XPS) and resistivity. TEM revealed that bioactive films were nanocrystalline with a grain size of the order of 15 nm and the presence of twins. Surface morphology studies before and after dissolution suggested that bioactive films released silver at therapeutic levels in the form of nano-particles or grains. Chemical species identification with XPS showed that the biologically active films were metallic in nature. The importance of oxygen in the sputtering environment, the resultant nanostructure and presence of twins are discussed to explain the unique antimicrobial properties of these silver films.

Bulk Metallic Glasses: Mechanical Behaviors

Sponsored by: The Minerals, Metals and Materials Society, TMS Structural Materials Division, TMS/ASM: Mechanical Behavior of Materials Committee
Program Organizers: Peter K. Liaw, University of Tennessee; Raymond A. Buchanan, University of Tennessee

Monday PM — Room: 217B
March 13, 2006 — Location: Henry B. Gonzalez Convention Ctr.

Session Chairs: Raymond A. Buchanan, University of Tennessee; Akiko Inove, Tohoku University

2:00 PM Keynote
Improved Mechanical Properties of Bulk Glassy Alloys Containing Spherical Pores: *Akihisa Inoue*[1]; T. Wada[1]; [1]Tohoku University

For future extension of application fields for bulk glassy alloys, it is important to develop a new type of glassy alloy which exhibits simultaneously high strength, low Young's modulus, large elastic elongation, high ductility, high corrosion resistance, low specific weight, high specific surface area and three dimensional bulk form etc. Considering that bulk glassy alloys in non-ferrous metal base systems possess unique characteristics of high strength, low Young's modulus, large elastic elongation, high fracture toughness and high corrosion resistance, the bulk glassy alloys are expected to become an important candidate material after the above-described modifications for alloy component and material surface morphology. One of the ways to develop a new material with the above-described properties is to fabricate ductile bulk glassy alloys containing open or closed pores in a wide range of volume fraction. Little is known about mechanical properties of porous bulk glassy alloys.

2:30 PM Invited
Flow and Fracture Studies on Bulk Metallic Glasses and Composites: *John J. Lewandowski*[1]; [1]Case Western Reserve University

The effects of systematic changes in stress state on the flow and fracture behaviour of a number of different BMGs and composites are being determined. In addition to conducting tension and compression tests with constant levels of confining pressure at different test temperatures, notched specimens are additionally being conducted under similar conditions in order to cover a broader range of stress states. Following a summary of these tests, the effects of changes in alloy chemistry and annealing on the fracture behaviour of a wide range of BMGs will be presented. Correlations of the fracture behaviour with changes in elastic constants will be demonstrated.

2:55 PM Invited
Experimental and Computational Investigation of Structure and Plastic Flow in Bulk Metallic Glasses: Matthew J. Lambert[1]; Wolfgang Windl[1]; *Katharine M. Flores*[1]; [1]Ohio State University

Improving the structural reliability of bulk metallic glass components requires a detailed understanding of the relationship between glass structure and plastic flow behavior. We examine the flow-induced structural changes in a Zr-based bulk metallic glass using a variety of experimental techniques, including positron annihilation spectroscopy. These results indicate a shift in the size distribution of flow defects after inhomoge-

neous flow consistent with the coalescence of free volume into nanovoids. The atomistic structure of several multicomponent glasses was further investigated through molecular dynamics simulations using EAM potentials. We employ a novel annealing technique that allows us to simulate extremely slow quench rates to produce glassy structures. Radial distribution functions of the modeled systems exhibit excellent agreement with experimental data. Comparing the detailed features of the nearest-neighbor order with experimental critical cooling rate data, we establish a set of criteria to predict the effect of changes in composition on glass forming ability.

3:20 PM Invited

Mechanical Properties and Devitrification Behavior of Cu-Zr-Ti-NM (NM-Noble Metals) Bulk Glass-Forming Alloys: *Dmitri Louzguine*[1]; Akihisa Inque[1]; [1]Tohoku University

A nanoscale icosahedral phase was recently obtained in a Cu55Zr30Ti10Pd5 bulk glass-forming alloy. The present work is devoted to an investigation of the formation kinetics, stability and homogeneity area of the nanoscale icosahedral phase formed on heating in the Cu-Zr-Ti-Pd system. Mechanical properties of the studied alloys will be reported. The Cu-Zr-Ti-Pd icosahedral phase is not a Cu-rich part of the compositional homogeneity area of the Zr-Cu-Pd one. Nanoscale icosahedral phase has chemical composition close to that of the alloy composition. The possibility for the Cu-Zr-Ti-Pd icosahedral phase of being a Cu-rich part of the compositional homogeneity area of the Zr-Cu-Pd one is ruled out. Moreover, Ti is found to be important element stabilizing quasicrystalline phase in the Cu-Zr-Ti-Pd alloys. Formation criteria for Cu- and Zr/Hf-based icosahedral phases are discussed based on quasilattice constant to average atomic diameter ratio. Deviation from this criterion leads to destabilization of the icosahedral phase.

3:45 PM Invited

Evolution of Mechanical Properties of Cast Zr-Cu-Al Glassy Alloys by Anneal Treatment: *Yokoyama Yoshihiko*[1]; Akihisa Inoue[1]; Peter K. Liaw[2]; Raymond A. Buchanan[2]; [1]Institute of Materials Research; [2]University of Tennessee

The volume of quenched glassy alloy is a variable of cooling rates during amorphization. Hence a change in the volume caused by structural relaxation can be regarded as a degree of amorphousness. The density of ternary eutectic Zr50Cu40Al10 bulk glassy alloys (BGAs) increases linear with annealing temperature below glass transition temperature (Tg). With annealing temperature, tensile strength and Vickers hardness show constant values, whereas the Young's moduli and Charpy impact values become larger and smaller, respectively. Charpy impact values of Zr-Cu-Al BGAs have a linear relationship with relative value of excess free volume. However, off eutectic BGAs in Zr-Cu-Al system exhibit different features changes with structural relaxation. Especially, Zr-enriched compositional BMGs show opposite features change against the eutectic BMG during structural relaxation. As a conclude, we can control the glass structure of cast Zr-Cu-Al BGA using a combination of compositional control and after anneal treatment below Tg.

4:10 PM Break

4:20 PM

Fatigue Behavior of Bulk Metallic Glasses: Role of Free Volume: *Jamie J. Kruzic*[1]; Maximilien E. Launey[1]; Ralf Busch[1]; [1]Oregon State University

Structural differences, such as the amount of free volume, affect the properties of bulk metallic glasses. Thus, a thorough understanding of the relationships between the amorphous structure and the mechanical properties is needed for these materials to achieve widespread use as structural materials. The cyclic fatigue behavior of several zirconium based amorphous alloys were investigated where the composition was held constant while the amount of free volume was varied. Free volume differences were quantified based on enthalpy recovery experiments and were achieved by 1) using different initial processing conditions or 2) by annealing to allow structural relaxation without crystallization. Significant improvements in the measured fatigue lives were found with lower amounts of free volume, even when the materials were in the as cast state. Such differences are considered in terms of how free volume changes affect each of the individual stages of the fatigue life and the associated salient mechanisms.

4:40 PM

The Effect of Frequency on Fatigue Behavior of Bulk Metallic Glass and Composites: *Gongyao Wang*[1]; P. K. Liaw[1]; A. Peker[2]; Y. Yokoyama[3]; M. Freels[1]; W. H. Peter[1]; R. A. Buchanan[1]; C. R. Brooks[1]; [1]University of Tennessee; [2]LiquidMetal Technologies Inc.; [3]Advanced Research Center of Metallic Glasses

LM001 and LM002 are commercial Zr-based bulk-metallic glasses (BMGs). The X-ray diffraction results and optical morphology show that LM001 is a monolithic BMG and LM002 is a BMG composite containing crystalline phases. The high-cycle-fatigue (HCF) experiments were conducted at different frequencies, using an electrohydraulic machine with a R ratio of 0.1 and under tension-tension loading, where $R = \sigma_{min.}/\sigma_{max.}$, $\sigma_{min.}$ and $\sigma_{max.}$ are the applied minimum and maximum stresses, respectively. The fatigue-endurance limit (265 MPa) of LM002 was found to be significantly lower than that (630 MPa) of LM001 at a frequency of 10 Hz. Changing the test frequency has no obvious effect on the fatigue behavior of LM001, but it seems that the lifetime of LM002 at the high stress level is lower at a high frequency than that at a low frequency. A mechanistic understanding of the fatigue behavior of the Zr-based BMGs is suggested.

5:00 PM

Effect of Nano Crystallites on the Deformation and Mechanical Behavior of a Nano Crystallite/Amorphous Matrix Composite: An Atomistic Simulation Study: *Young-Min Kim*[1]; Byeong-Joo Lee[1]; [1]Pohang University of Science and Technology

It is known that mechanical properties of amorphous materials can be further improved by promoting homogeneous precipitation of nano crystallites within the amorphous matrix. Though lots of investigations have been done on the deformation and mechanical behaviors of the nano crystallite/amorphous matrix composite, details of the effect of nano crystallites on those properties are not known yet. In this study, we investigated the effects of embedded pure Cu crystallites on the deformation and mechanical behavior of a nano crystallite/Cu-Zr amorphous matrix composite, by using a molecular dynamics simulation study. We focused on the amount of contribution of the nano crystallites to flow stress and overall deformation during a compression and a tensile test. The role of interfaces between crystallites and matrix on the mechanical behavior and the validity of the rule of mixture which is frequently used to estimate overall physical properties of composite materials will also be discussed.

5:20 PM

High Temperature Deformation Behavior of In-Situ Bulk Metallic Glass Matrix Composites: *Xiaoling Fu*[1]; Yi Li[1]; Christopher Schuh[2]; [1]National University of Singapore; [2]Massachusetts Institute of Technology

Macroscopic ductility is promoted in bulk metallic glasses by both composite reinforcements (at low temperatures) and by the activation of viscous flow mechanisms (at high temperatures). It is of fundamental interest to understand deformation physics when both of these strategies are employed at the same time. Despite the quickly growing literature around the room-temperature mechanical properties of metallic glass matrix composites (MGMCs), the deformation behavior of MGMCs over a wide range of temperatures and strain rates has yet to be systematically investigated, especially at high temperatures close to Tg. Here the high temperature compressive behavior of both Zr-based and La-based MGMCs with in-situ reinforcements is explored systematically over a series of strain rates. Additionally, the volume fraction of second-phase reinforcements was tailored to explore its effect on both inhomogeneous and homogeneous deformation modes.

5:40 PM

High Temperature Mechanical Behavior of Mg-Based Amorphous Alloys Produced by Low-Pressure Die-Casting: *Bulent Gun*[1]; Kevin Laws[1]; Michael Ferry[1]; [1]University of New South Wales

Using a novel preparation technique, tensile samples of die-cast Mg-Cu-Y amorphous alloys were produced in compliance with ASTM E8-04 for determining elevated-temperature mechanical behaviour. The as-cast microstructures were examined initially by XRD and TEM which confirmed the amorphous nature of the alloys. Prior to mechanical testing, DSC and XRD were carried out to determine the various critical tempera-

tures (glass transition, crystallization and melting temperatures) of each alloy, and to generate reliable static crystallization maps. The flow behaviour of the alloys was investigated at various temperatures in the supercooled liquid region at strain rates ranging from 0.001 to 0.1/s. The mechanical data were used to compute the strain rate sensitivity and other flow characteristics of the alloys. For a given set of testing conditions, samples were deformed to a range of strains and examined using various techniques to highlight the substantial influence of deformation on crystallization behaviour.

Carbon Technology: Anode Raw Materials

Sponsored by: The Minerals, Metals and Materials Society, TMS Light Metals Division, TMS: Aluminum Committee
Program Organizers: Morten Sorlie, Elkem Aluminium ANS; Todd W. Dixon, Conoco Phillips Venco; Travis J. Galloway, Century Aluminum Company

Monday PM Room: 8A
March 13, 2006 Location: Henry B. Gonzalez Convention Ctr.

Session Chair: James B. Metson, University of Auckland

2:00 PM
Viscosity Modification and Control of Pitch: *Melvin D. Kiser*[1]; M. B. Sumner[1]; B. K. Wilt[1]; D. Chris Boyer[1]; [1]Marathon Petroleum Company, LLC

The addition of low concentrations of certain oxygenated compounds, particularly esters, to bitumen has been shown to have a profound effect on viscosity. The bitumen in question includes but is not limited to petroleum pitch, coal tar pitch and asphalt cements. A cost effective source of esters has been found to be biodiesel. This paper will provide general information on biodiesel and detail its effect on the viscosity of pitch as a function of concentration. Other topics of discussion are effects on other properties of the bitumen as well as a method of detection and control of ester concentration in the final product.

2:25 PM
Laboratory Anode Comparison of Chinese Modified Pitch and Vacuum Distilled Pitch: John Thomas Baron[1]; *Robert H. Wombles*[1]; [1]Koppers Industries Inc

The process currently used to produce the large percentage of 100°C to 110°C softening point anode binder pitch in China today is a heat treating process which produces a product called modified pitch. Modified pitch has all the characteristics of a pitch produced by heat treatment including 3% to 10% mesophase content. The presence of mesophase in binder pitch introduces problems with binder pitch and coke mixing and the resultant properties of the baked anode. This paper will present the results of a laboratory anode study comparing the properties of laboratory anodes produced with Chinese modified pitch and Chinese vacuum distilled pitch. The results indicate that the use of vacuum distilled pitch results in significant improvements in anode properties.

2:50 PM
Composition and Intermolecular Reactivity of Binder Pitches and the Influence on Structure of Carbonized Pitch Cokes: *Harald A. Oye*[1]; Stian Madshus[1]; Trygve Foosnaes[1]; Margaret Hyland[1]; Jostein Krane[1]; [1]Norwegian University of Science and Technology

Hydrogen donor and acceptor abilities for a series of coal-tar and petroleum pitches have been determined as a measure of the intermolecular reactivity. The carbon disulphide soluble part has also been investigated by NMR in order to identify and quantify structures that are considered to either increase or decrease the reactivity. The properties differentiated the pitches studied and were found to correlate with the amount of volatiles released during the critical stages of carbonization. A link was found between the hydrogen transfer properties of the petroleum pitches and the size of optical texture of the resulting cokes. However, for pitches of coal-tar origin the presence and amount of particulate matter (QI) was found to be the most influential factor on the size of the optical texture.

3:15 PM
Vertical Stud Soderberg Emissions Using a Petroleum Pitch Blend: *Euel R. Cutshall*[1]; Linda Maillet[1]; [1]Alcoa Inc

At the Alcoa La Coruna Plant in Spain organic emissions and worker exposure levels were determined and compared for individual cells using 100% coal tar pitch and a coal tar/petroleum pitch blend. Advantages and limitations of using the coal tar/petroleum pitch blend are discussed.

3:40 PM Break

3:55 PM
Characterization of Green Anode Materials by Image Analysis: *Stein Rørvik*[1]; Arne Petter Ratvik[1]; Trygve Foosnæs[2]; [1]Sintef Materials and Chemistry; [2]Norwegian University of Science and Technology

A method to characterize green (unbaked) carbon composite materials has been developed. The method is based on computer-automatized microscopy and digital image analysis. A reproducible procedure for sample preparation has been developed, as well as a method for distinguishing the pitch from the coke grains and the pores in the microscope images. The method has been used to examine the distribution of the pitch, pores and coke grains in carbon anode samples. The method has been applied to both laboratory made and industrial materials. Focus has been on anodes for aluminium production, but the method can also be used for cathodes and other composite carbon materials. This paper explains the principles of the method and presents results from analysis of anodes with variations in binder (pitch) content and coke grain size.

4:20 PM
Neural Network in Automatic Process Control System of Coke Calcination: *Vitaly Sinelnikov*[1]; [1]RUSAL Engineering and Technological Center

Automatic process control system of coke calcination consists of two levels. Control, data transmission and digital control of the kiln temperature conditions are done with the help of regulators on lower level. Upper level of the kiln automatic process control system consists of two principal sublevels: visualization system of calcination; neural models of forecast and control (changes in regulator setpoints of kiln). Neural network of general regression was chosen as the calcination model. Genetic cone-type algorithm was used for adjustment of network weights. The task of change in regulator setpoints is narrowed down to the task of optimization theory. Necessity in the implementation of control neural network system consists in fact that regulators alone can not provide accuracy response to changing process parameters because their mathematical algorithm is destined for control by target (regulator setpoint) and not by operational change of target depending on the changing process parameters.

Cast House Operations: Session I

Sponsored by: The Minerals, Metals and Materials Society, TMS Light Metals Division
Program Organizers: Rene Kieft, Corus Group; Travis J. Galloway, Century Aluminum Company

Monday PM Room: 7D
March 13, 2006 Location: Henry B. Gonzalez Convention Ctr.

Session Chair: Helmut Suppan, AMAG Rolling GmbH

2:00 PM Introductory Comments

2:10 PM
A Study on the Failure Investigation of Graphite Column Used for Degassing in the Aluminum Caster Plant: *Y. V. Ramana*[1]; Rajnish Kumar[1]; [1]Hindalco Industries Ltd

A graphite agitator is used for purging chlorine to expel entrapped gases from molten aluminium metal in the Caster Plant process of Hindalco. Uncertainty in life span of the column of the agitator was adversely affecting the production planning activities and operational efficiency. To find out reasons for inconsistency in the life span, a systematic study was conducted on physical, chemical and microstructural parameters using failed samples of life span ranging from a few hours to several days. The predominant reasons observed for failure are porosity and internal voids/

cracks. It was observed that larger pores and increasing porosity is facilitating rapid oxidation of graphite at elevated temperatures hence the early failure. This phenomenon is prevalent particularly at the region of metal-air interface and above of the graphite column where frequent failure was experienced. The column submerged in molten metal is found to be less susceptible for such failures.

2:40 PM

Building the Billet Production Management Process at Alcoa Pocos De Caldas: *Andre Luis Trópia de Abreu*[1]; Leonardo Paulino[1]; [1]Alcoa Alumínio SA

An issue that comes challenging the actors involved on worldwide aluminum production is how to manufacture a billet that result in a good extrusion performance. The answer to it involves the establishment of measurable quality requirements. On this picture the traditional quality requirements utilized at Alcoa Poços – chemical composition and superficial finishing – can not measure enough the final performance of the process control activities. The change starts with the intensification of the discussion between Alcoa and its customers – Alcoa Extrusion Plants – in order to better understand its needs and creating empathy. The evolution of the discussion creates an appropriate condition to revise the billet quality requirements. On this way, metallographic measures are included to this set to sustain further aluminum billets process developments.The recognition and credibility of the new set of requirements gives objectivity on the supply-customer connection with a regular performance measurement basis.

3:10 PM

Quantifying Factors Affecting Aluminum In-Line Degassing Efficiency: *David W. Busch*[1]; [1]Pyrotek Inc

Extensive plant data taken from two significantly different aluminum alloys produced in three different SNIF degassing units was analyzed to help quantify the effects of atmospheric humidity and other operating parameters on dissolved hydrogen removal. Absolute humidity increased by an average of 54% during the summer months in one location while aluminum post-treatment hydrogen level increased on average by 20%. Techniques are discussed which can be employed to increase hydrogen removal efficiency and mitigate the effects of high humidity. Data collected during formal degasser acceptance testing is also presented where sodium and inclusion removal and dross formation is evaluated.

3:40 PM Break

4:00 PM

A Case Study on Failure Analysis of AA 6063 Billets during Extrusion Process: *Y. V. Ramana*[1]; Rajnish Kumar[1]; Naresh Kumar Singh[1]; [1]Hindalco Industries Ltd

Hindalco produces Wagstaff billets of aluminium alloys for downstream processing by different customers. A typical case of frequent failure of AA6063 billets at the customer's end during extrusion process was observed. Failure was due to sagging and breaking of billet after preheating and during extrusion process. To find out the reasons of failure, a systematic comparative study was conducted using as supplied and failed samples. PoDFA analysis and chemistry of the supplied material showed no significant reason for failure. On the other hand, macro and microstructural analysis of the samples revealed interesting observations like rosette formation, grain boundary melting, eutectic and script like structures in the preheated billet samples. These observations indicate that the failure is the result of overheating and liquidation of the metal during preheating process.

4:30 PM

Metal Quality of Secondary Alloys for Al Castings: *Eulogio Velasco*[1]; [1]Nemak

High mechanical properties, fatigue, pressure tight and low porosity are requirements of aluminum cylinder heads and blocks related with the quality of liquid metal. With secondary alloys can be possible to reach these characteristics. Several control stages are necessary from row material (Al scrap) to final stage: liquid metal in the holder furnace. In order to measure the quality of liquid metal, several samples with the PreFil®-Footprinter Unit were taken along the route of melting process. The tracking of the process include melting at reverberatory furnace, fluxing, liquid treatment and degassing. The results showed areas to improve with operational practices and new degassing equipments and use of fluxes treatment.

Cast Shop Technology: Furnace Operation and Refractory Materials

Sponsored by: The Minerals, Metals and Materials Society, TMS Light Metals Division, TMS: Aluminum Committee
Program Organizers: Rene Kieft, Corus Group; Gerd Ulrich Gruen, Hydro Aluminium AS; Travis J. Galloway, Century Aluminum Company

Monday PM — Room: 7C
March 13, 2006 — Location: Henry B. Gonzalez Convention Ctr.

Session Chair: Gerd Ulrich Gruen, Hydro Aluminium AS

2:00 PM

Calcium Aluminate Based Castables for Liquid Aluminium Contact Areas – A Laboratory Evaluation: *Marcel Hogenboom*[1]; [1]Corus

Recently calcium hexaluminate (CA6) was introduced as a new synthetic dense refractory aggregate for refractories. Regarding the chemical composition and claimed low wetability by molten aluminium calcium hexaluminate is an interesting aggregate. Refractory materials based on this aggregate can be a solution for application areas suffering from aluminium penetration and corundum growth. Since the introduction of this aggregate several refractory suppliers introduced a castable based on calcium hexaluminate on the market. A selection of those commercially available castables is characterised and tested in the laboratory on relevant properties in respect to potential application areas. In this paper the results of the tests performed are presented and discussed.

2:25 PM

Computational Analysis of the Conversion of Generic Aluminum Holding Furnace from Air-Fired to Oxy-Fired Burners: *Brian Golchert*[1]; Ashwini Kumar[1]; Hossam Metwally[1]; [1]Fluent, Inc.

Many of the gaseous emissions from aluminum furnaces are caused by the use of air as the oxidizer of the fuel. If air were to be replaced by nearly pure oxygen, the volume of greenhouse gas emissions would be drastically reduced. The purpose of this study was to use computational fluid dynamics to model the effect of changing a generic aluminum holding furnace from air-fired to oxy-fuel fired burners. Initially, two cases were created: a base case with air-fired burners and then a case with oxy-fuel burners located in the same position as the air-fired burners with the same natural gas flow rate. The oxy-fuel case produced flue temperatures that were different than the air-fired case so several additional computational cases were created to try and match the air-fired flue temperature. This paper will present the results of this study and will discuss the advantages/disadvantages of converting to oxy-fuel.

2:50 PM

Design Considerations for Charge Preheating Ovens: *Jan Migchielsen*[1]; Jan De Groot[1]; [1]Thermcon Ovens BV

Driven by valid safety concerns, more and more cast houses install preheating ovens for pre-heating and drying of sows, ingots and scrap before charging into a melting furnace. While preheating of the furnace charge enhances safety and improves fuel consumption at the same time, there are issues that must be addressed to avoid introducing new safety hazards. Special attention must be paid to issues like aluminium dust and combustible contaminants of materials that are charged into a preheating oven as these ovens start their cycle at a temperature well below the auto ignition temperature. Using a preheating oven without the proper technical considerations may therefore lead to exchanging one risk for the other. This paper addresses the design considerations that lead to safe and efficient installations for optimum pre-heating of scrap prior to melting.

3:15 PM Break

3:30 PM

Flame-Object Heat Transfer Using Different Burner Types and Orientations: Geza Walter[1]; *Laszlo Istvan Kiss*[1]; Andre Charette[1]; Vincent Goutiere[2]; [1]Université du Québec à Chicoutimi; [2]Alcan International

Gas fueled burners are frequently used as heat sources in metallurgy. The heat transfer between the flame and charge in a furnace depends on the type of the burner, its adjustment as well as on its position and orientation relative to the charge. An experimental study was performed in order to clarify the effects of burner and flame types and flame-object geometry on the heat transferred to the charge as well as on the mechanism of the heat transfer. The methodology and the results of flame object interaction in the case when firing is parallel to the horizontal surface of the charge were presented earlier. In the present paper the case of impingement by inclined burners and partial impingement on the corner of a solid charge will be shown. The study is completed with the analysis of the temperature and velocity fields in the gas phase around the objects.

3:55 PM

Melt Down Dross on Magnesium Containing Aluminum Alloys: *John A. Clark*[1]; [1]U.S. Department of Energy

Dross is present on molten baths of aluminum alloy immediately after the remelt of ingots. Semi-quantitatively, prime (unalloyed) aluminum is known to produce very little dross during meltdown, while alloys containing significant additions of magnesium produce much dross. The Albany Research Center (U.S. Department of Energy) developed and operates the Laboratory Scale Reverberatory Furnace (LSRF) which is capable of melting and holding approximately 200 pounds of aluminum. Magnesium containing and prime aluminum alloys have been melted in the LSRF. This paper will generically identify the weight of dross present on aluminum baths of various magnesium contents immediately after meltdown in the LSRF relative to the weight of ingot material charged. Melts in the LSRF have demonstrated dross on prime aluminum ingots of less than 1%. Ingots of aluminum-magnesium alloy have demonstrated 10% dross by weight. Possible correlation between magnesium content and dross formation will be examined.

Characterization of Minerals, Metals and Materials: Ceramic and Refractories

Sponsored by: The Minerals, Metals and Materials Society, TMS Extraction and Processing Division, TMS: Materials Characterization Committee

Program Organizers: Jiann-Yang James Hwang, Michigan Technological University; Arun M. Gokhale, Georgia Institute of Technology; Tzong T. Chen, Natural Resources Canada

Monday PM — Room: 206A
March 13, 2006 — Location: Henry B. Gonzalez Convention Ctr.

Session Chairs: Jiann-Yang James Hwang, Michigan Technological University; Sergio Neves Monteiro, State University of the Northern Rio de Janeiro

2:00 PM

Characterization of Ceramic Foam: *Sergio Neves Monteiro*[1]; Carlos Maurício Fontes Vieira[1]; [1]State University of the Northern Fluminense

In the present work, a ceramic foam elaborated with illitic clays was characterized. Properties related to density and compression strength were determined in samples fired at 1300°C, a temperature that permits the clay structure to eliminate and retain gases that will produce the foamy structure. The microstructure of the ceramic foam was studied by X-ray diffraction, scanning electron microscopy and mercury porosimetry. The results showed that the ceramic foam presents a bulk density of 0.38 g/cm3. The microstructure is formed by large open pores, quartz particles and vitreous phase.

2:25 PM

Fibrous Reinforcement in Clay-Bonded Silicon Carbide Refractory Using Andalusite Powder: *Bowen Li*[1]; Jiann-Yang James Hwang[1]; Shangzhao Shi[1]; [1]Michigan Technological University

Silicon Carbide is an excellent refractory material due to its high melting temperature, excellent thermal conductivity, low thermal expansion, and consequently its good thermal shock resistance. In addition, the high hardness, corrosion resistance and stiffness lead to a wide range of applications where wear and corrosion resistance are primary performance requirements. Commercial silicon carbide refractory is frquently manufctured by bonding silicon carbide particles with clay to provide the green strength and to aid the sintering. However, clay may cause shrinkage, fracture, and thermal shock problems on the products. This study investigate the potential of replacing a portion of clay with the andalusite powder. The results show that micron size andalusite powder can improve not only the strength of refractory but also the sinterability. The mechanisms for the improvements are discussed.

2:50 PM

Characterization of Post-Mortem Refractory Ceramics from Special Al-Metal Alloy and Super-Alloy Melting Furnaces: *Musa Karakus*[1]; William L. Headrick[1]; Eric L. Feiner[1]; [1]University of Missouri-Rolla

Refractory ceramic linings of special metal and super alloy melting vessels as well as submerged molten-metal handling refractory ceramics are subjected to significant chemical corrosion and mechanical wear/abrasion during melting. The corrosion and wear of refractories results in energy losses and frequent replacement and repair. Study of post-mortem materials provides better understanding of the mechanisms of chemical attack. The chemical attack is identified to be very similar to reactive metal penetration, in which silica component is reduced by liquid aluminum penetration in special Al-alloy melting process. The failure of refractory lining in super alloy melting is identified to be due to thermal spalling, metal penetration and slag attack.

3:15 PM

Characterization of Clayey Ceramic Body Used for Roofing Tile Fabrication: *Carlos Maurício Fontes Vieira*[1]; Patrícia Machado Andrade[1]; Enio Vaz Silva[1]; Jonas Alexandre[1]; Sergio Neves Monteiro[1]; [1]State University of the Northern Fluminense

In the present work a ceramic body, elaborated with mixture of clays and sand, used for roofing tiles produced in Campos dos Goytacazes, north of the State of Rio de Janeiro in Brazil, was characterized. Characterization was done by X-ray diffraction, thermo analysis, chemical composition, particle size distribution and plasticity. In addition, technological properties related to water absorption, linear shrinkage and flexural rupture strength were determined in samples fired at 700, 900 and 1100°C. The results showed that the investigated ceramic body has satisfactory plasticity and present a refractory behavior in association with firing due to the predominantly kaolinitic nature of the clays.

3:40 PM Break

3:50 PM

Application of Cathodoluminescence (CL) Microscopy and Spectroscopy to Refractory Raw Minerals and Ceramics: *Musa Karakus*[1]; [1]University of Missouri-Rolla

In this study, a unique characterization technique, cathodoluminescence (CL) microscopy and spectroscopy used in conjunction with reflected light (RL) microscope is described and its applications to wide variety of refractory raw minerals and ceramics are demonstrated. The application of CL microscopy and spectroscopy to refractory ceramics is very comprehensive because almost all thermally processed refractory starting materials and refractory ceramics cathodoluminesce spectacularly, i.e., they display characteristic CL colors when bombarded by electrons. Only phases high in Fe2+ will not yield sufficient CL information to allow full application of the method. The CL images and spectra for Al2O3, MgO, MgAl2O4, ZrO2, Y2O3, AlN, SiAlON, SiC, are obtained. The CL method is proven to be extremely useful for characterizing refractory ceramics.

4:15 PM

Characterization of Steel Slag for Incorporation into Red Ceramics: Sergio Neves Monteiro[1]; Stelamaris Chaves Intorne[1]; Dylmar Penteado

Dias[1]; Elias Lira dos Santos Junior[1]; *Carlos Maurício Fontes Vieira*[1]; [1]State University of the Northern Fluminense

This work had as its objective the characterization of a waste, steel slag, generated from integrated steel plant with a view to its recycling into red ceramics fabrication. The characterization was performed in terms of chemical composition by X-ray fluorescence (XRF), particles size distribution, X-ray diffraction (XRD), thermal analysis (DTA/TG) and scanning electron microscopy (SEM). The results indicate that the steel slag presents high amount of Ca, Fe, Mg and Si. The weight loss of the steel slag at temperatures above 800ºC is associated with calcium carbonate decomposition. The coarse particle size of the steel slag is inadequate for its direct recycling into red ceramic fabrication. As a possible solution, it suggested that screening or grinding the steel slag to a convenient particle size distribution would alloy its successful industrial incorporation into red ceramic products.

4:40 PM

Phase Transformation of Andalusite and Its Impacts on Refractory Brick Reinforcement: *Bowen Li*[1]; Jiann-Yang James Hwang[1]; Zhiyong Xu[1]; [1]Michigan Technological University

Andalusite is an excellent raw material for refractory applications due to its high aluminum oxide content and phase transformation to mullite at high temperature. Traditionally granular andalusite in particle sizes of about 1 to 2 mm was used to produce refractory brick. This study shows that, if powder andalusite in micron particle size is utilized to replace the granular andalucite, reinforement on the refractory brick can be obtained and the sintering temperature can be reduced. The phase transformation of powder andalusite plays a key role for the difference.

5:05 PM

Characterization of the Ceramic Material for High Pressure Applications: Alan Monteiro Ramalho[1]; Guerold Sergevitch Bobrocnitchii[1]; *Sergio Neves Monteiro*[1]; Ana Lucia Diegues Skury[1]; [1]UENF

In the synthesis and sintering process to obtain superhard materials, such as diamond and cubic BN, deformable ceramic capsules are used as gasket to transmit an support the required high pressures and high temperatures. The ceramic material should have special physical and chemical charcateristics, such as refractoriness, shear strength and compressibility. In this work Brigdman type anvils, made of hard metal or tool steel, were used to characterize gaskets made of calcite as function of the maximum compressible tchickness. Tests were performed with different polymers as binding medium for the calcite powder. Chemical analysis by EDS/SEM and X-ray fluorescence was also performed. The results showed that braziliam calcite can be sucessfully used in the fabrication of gaskets.

Computational Thermodynamics and Phase Transformations: Atomic Modeling Based Alloy Thermodynamics II

Sponsored by: The Minerals, Metals and Materials Society, TMS Electronic, Magnetic, and Photonic Materials Division, TMS Materials Processing and Manufacturing Division, TMS Structural Materials Division, TMS: Chemistry and Physics of Materials Committee, TMS/ASM: Computational Materials Science and Engineering Committee
Program Organizers: Dane Morgan, University of Wisconsin; Corbett Battaile, Sandia National Laboratories

Monday PM — Room: 210A
March 13, 2006 — Location: Henry B. Gonzalez Convention Ctr.

Session Chairs: Isao Tanaka, Kyoto University; Axel Van de Walle, Northwestern University

2:00 PM Invited

High-Throughput Measurements as Inputs to Computational Thermodynamics: *Ji-Cheng Zhao*[1]; Xuan Zheng[2]; David G. Cahill[2]; [1]General Electric Company; [2]University of Illinois, Urbana-Champaign

This talk will illustrate the use of diffusion multiples and micro-scale property probes to map phase diagrams, thermal conductivity, and specific heat capacity. The information can be used as inputs to computational thermodynamics. Phase diagrams are essential input to CALPHAD modeling. The diffusion-multiple approach can map phase diagrams at an efficiency orders-of-magnitude higher than that using individual equilibrated alloys. Micro-scale thermal conductivity measurements on compositional gradients in diffusion couples/multiples can be used to evaluate compositional point defects such as vacancies and anti-sites and to study ordering effects and site preference (elemental substitution) in intermetallic compounds. All the information are important for modeling the thermodynamics, especially for selecting the right sublattice models. Micro-scale specific heat measurements can provide direct inputs to CALPHAD modeling. Examples will be used to illustrate the methodologies.

2:30 PM Invited

Crystallographic Data for Non-Organic Materials: *Vicky Lynn Karen*[1]; [1]National Institute of Standards and Technology

Crystallographic data models are used on a daily basis to visualize, explain, and predict the behavior of chemicals and materials. Access to reliable information on crystallographic structure helps researchers concentrate experimental work in directions that optimize the discovery process. In partnership with outside organizations, the National Institute of Standards and Technology (NIST) has extended its crystallographic data program to provide evaluated full structural data for all non-organic materials including inorganics, metals, minerals and ceramics. The Inorganic Crystal Structure Database (ICSD) contains full structural and bibliographic information for more than 80,000 structures; the NIST Structural Database (metals, intermetallics) ~ 60,000 entries. Over recent years, NIST and its partners have been building a modern infrastructure for its databases. This has included a) re-evaluating and re-structuring existing and new database entries; b) developing software tools for the calculation and standardization of derived data items; c) developing modules for the intelligent access of these data; and d) providing access through modern user interfaces and networking capabilities. This presentation will focus on the database content, uses, and software tools to exploit the content of these data. Future directions include plans for interoperability between the non-organic crystal structure data, phase equilibria diagrams, and other NIST materials databases.

3:00 PM Invited

Materials Informatics: Knowledge Acquisition for Materials Design: *John Rodgers*[1]; [1]Innovative Materials Technologies, Inc

Combinatorial materials science methods are being used to synthesize, test, characterize and predict promising candidate materials for a number of applications in material science. These methods are producing enormous amounts of experimental, and derived, data that requires storage and analysis. Data mining provides exploration of this multidimensional chemical and property space, at a previously unavailable level of detail, and can rapidly estimate physical properties that are difficult to measure using experimental approaches. Given these vast resources of structure and property data it is possible to extract trends on the structure of materials and their properties and use these results in the materials design stages. These informatics approaches, coupled with ab initio quantum mechanics methodologies, provides many of the tools needed to guide materials selection via combinatorial materials science experiments.

3:30 PM Invited

A Practical Approach to the Prediction of Crystal Structure by Merging Data-Mining Methods with First Principles Quantum Mechanics: *Gerbrand Ceder*[1]; Chris Fischer[1]; Kevin Tibbetts[1]; Dane Morgan[2]; [1]Massachusetts Institute of Technology; [2]University of Wisconsin

The prediction of structure is a key problem in computational materials science. Traditionally, empirical rules have been extracted by observing trends in large amounts of experimental data. On the other hand, computational quantum mechanics is highly accurate in reproducing structural energy differences, but suffers from the difficulty that a global optimization can not really be performed in the physical space of atomic coordinates. As such, ab-initio energy calculations are usually only used to "verify" the relative energy of structures one might have guessed for a given chemical composition. In a departure from previous computational approaches, we combine data-mining to extract information from large amounts of experimental information and a database of over 15,000 first principles computations, with first principles computations to determine

energies. We show that this approach is highly efficient in finding the ground states of binary metallic alloys and can be easily generalized to more complex systems.

4:00 PM Break

4:10 PM Invited
Design of New Materials for Hydrogen Storage: *Blanka Magyari-Kope*[1]; Vidvuds Ozolins[1]; Christopher Wolverton[2]; [1]University of California, Los Angeles; [2]Ford Motor Company

Practical hydrogen storage for mobile applications requires sustainable materials that contain large amounts of hydrogen, have low decomposition temperatures and fast kinetics for absorption and desorption. Theoretical modeling employing quantum mechanics, can help improve the state-of-the-art in hydrogen storage properties by (1) providing insights into the underlying microscopic processes, (2) predicting new materials. One of the most promising classes for reversible hydrogen storage is represented by complex hydrides. In particular the group I, II and III elements Li, Na, Mg, B, Al, N form a large variety of metal-hydrogen complexes. We present systematic first-principles electronic structure calculations for a database of hydrides. Structural stabilities, electronic properties, thermodynamical properties and hydrogen-absorption enthalpies are determined, and structure-property relationships are discussed. These findings are expected to be useful in designing new materials of novel compositions, aimed to improve the hydrogen capacity at rational temperatures and pressures. Research supported by DOE Grant DE-FC36-04GO14013.

4:40 PM
First-Principles Calculations of Lattice Mismatch and Interfacial Energies between β''-Mg5Si6 and α-Al in Al-Si-Mg Ternary Alloys: *Yi Wang*[1]; C. Wolverton[2]; C. Ravi[2]; Z.-K. Liu[1]; L.-Q. Chen[1]; [1]Pennsylvania State University; [2]Ford Research and Advanced Engineering

The metastable β'' phase is often the most effective hardening precipitate in Al-rich Al-Mg-Si alloys. The amount of strengthening depends critically on the volume fraction, number density as well as the morphology of the precipitates. Two important factors that control the precipitate morphology are the lattice mismatch and the magnitude and anisotropy of interfacial energy between the precipitate and the matrix. In this work, first-principles supercell calculations are employed to calculate the β''/Al interfacial energies as well as the stress-free lattice parameters of the β'' phase. The three interfacial orientations are chosen based on existing high-resolution TEM observations: [230]Al$_{\|}$[100] β'', [001]Al$_{\|}$[010] β'', and [10]Al$_{\|}$[001] β''. The calculated interfacial energies, strain energies, and lattice mismatches for different interfacial orientations were analyzed and compared. The effect of atomic mixing across the [10]Al$_{\|}$[001] β'' interface is discussed. Finally, the interfacial and strain energies are used to estimate the equilibrium shapes for β'' precipitates.

5:00 PM
Pressure-Induced Spin Transitions in the (Fe_x,Mn_{1-x})S_2 System: *Kristin Aslaug Persson*[1]; Gerbrand Ceder[1]; Dane Morgan[2]; [1]Massachusetts Institute of Technology; [2]University of Wisconsin

Pressure-induced spin transitions of the Fe^{2+} and the Mn^{2+} ions in the (Fe_x,Mn_{1-x})S_2 system are investigated using calculations based on first-principles density-functional theory within the GGA+U formalism. Even though the transition pressures decrease with increasing Fe content, the volume change at the transition remains remarkably constant as long as both Fe and Mn participate. At high Fe content, transition pressures approaching zeroare obtained.

5:20 PM
Influence of Many Body Interaction on the Energetics and Dynamics of Metallic Nanoclusters: *Ho-Seok Nam*[1]; David J. Srolovitz[1]; [1]Princeton University

Metallic nanoclusters exhibit various structural modifications, for example, for fcc metals, cuboctahedra, decahedra, and icosahedra. The energetics and dynamics of nanoclusters was investigated as a function of bonding characteristics by employing a set of embedded atom method (EAM) potentials that can be adjusted to vary the many-body effects. With only pair interaction, icosahedral structure is energetically stable up to sizes N=3000. As the strength of many-body interaction increases, the crossover size decreases monotonically and icosahedra become metastable even for small clusters (less than 100 atoms). However, our molecular dynamics simulations on freezing of nanoclusters showed that most of clusters of a few hundred atoms were frozen to an icosahedral structure from liquid droplet in spite of its metastability. These results were compared with general trends of transition and noble-metal clusters in the literature.

5:40 PM
Application of the Cluster/Site Approximation to *fcc* Phases in Ni-Al-Cr System: Weisheng Cao[1]; *Jun Zhu*[1]; [1]University of Wisconsin

The Cluster/Site Approximation (CSA) has been used to model the *fcc* phases (disordered γ with A1 structure and ordered γ' with $L1_2$ structure) in the Ni-Al-Cr ternary system. The CSA takes into account short-range order (SRO), which is essential to satisfactorily describe the thermodynamics of order/disorder transitions such as occur between the *fcc* phases in the Ni-Al-Cr system. It possesses computational advantages over the Cluster Variation Method (CVM) while offering comparable accuracy in the calculation of multi-component phase diagrams. This makes the CSA a practical method for calculations on real alloy systems. These points are illustrated in the application of the CSA to *fcc* phases in the Ni-Al-Cr system. The CSA-calculated phase diagrams, which use fewer model parameters than used in previous descriptions, based on the point approximation, show good agreement with the experimental data. In addition, the *fcc* metastable phase diagrams show reasonable ordering/disordering behavior and phase relationships.

Deformation and Fracture from Nano to Macro: A Symposium Honoring W. W. Gerberich's 70th Birthday: Materials Properties: Testing and Techniques

Sponsored by: The Minerals, Metals and Materials Society, TMS Materials Processing and Manufacturing Division, TMS Structural Materials Division, TMS/ASM: Mechanical Behavior of Materials Committee, TMS: Nanomechanical Materials Behavior Committee
Program Organizers: David F. Bahr, Washington State University; James Lucas, Michigan State University; Neville R. Moody, Sandia National Laboratories

Monday PM — Room: 214D
March 13, 2006 — Location: Henry B. Gonzalez Convention Ctr.

Session Chairs: William D. Nix, Stanford University; Tim Foecke, National Institute of Standards and Technology

2:00 PM Invited
Nanomechanical Contact Studies of PDMS: Donna M. Ebenstein[1]; *Kathryn J. Wahl*[1]; [1]Naval Research Laboratory

The Johnson-Kendall-Roberts (JKR) theory of elastic contact is used to evaluate work of adhesion and modulus of elastomeric thin films. We present a comparison of five approaches to analyze quasi-static and dynamic JKR force curve data obtained using instrumented indentation. Indentation experiments were performed on poly(dimethylsiloxane) (PDMS) samples (E < 10 MPa) with a 200 μm radius glass sphere. Direct curve fitting as well as simplified 2- and 3-point analysis methods were used to compare modulus values determined from load-displacement and stiffness-load data. Simple curve fit methods not requiring determination of the tip-sample contact point ("zero" displacement) provided modulus values closest to those obtained by direct curve fitting. The dynamic stiffness-load data revealed a frequency dependent modulus; simultaneous load-displacement measurements were consistent with the relaxed, or low-frequency, modulus of the PDMS sample. Hence, both the frequency dependent and relaxed modulus can be obtained from a single measurement.

2:20 PM
Nanoindentation Behavior of Ultrathin Polymeric Films: *Kebin Geng*[1]; Fuqian Yang[1]; Thad Druffel[2]; Eric A. Grulke[1]; [1]University of Kentucky; [2]Optical Dynamics Corporation

Measurement of the mechanical properties of ultrathin polymer films is important for the fabrication and design of nanoscale layered materials. Nanoindentation was used to study the viscoelastic deformation of ultrathin polymeric films with thicknesses of 47 nm, 125 nm and 3000 nm. The reduced contact modulus increases with the indentation load and penetration depth due to the effect of substrate, which is quantitatively in agreement with an elastic contact model. The flow of the ultrathin films subjected to constant indentation loads is shear-thinning and can be described by a linear relation between the indentation depth and time with the stress exponent being 1/2.FY is grateful for support from NSF grant DMR-0211706 and support from General Motors Corporation. KG and EG are grateful for support from Optical Dynamic Corporation.

2:35 PM

Electrical Property Measurements of Stressed Dielectric Films Using Nanoindentation: *John M. Jungk*[1]; Michael T. Dugger[1]; Somuri V. Prasad[1]; [1]Sandia National Laboratories

Microsystem-based radio frequency switches allow for lower static power dissipation than existing solid-state switches, but charging and changes in the contacting surfaces can cause a drift in actuation voltage and decrease in reliability of capacitively switched devices. Potential relationships between contact stress and electrical response have yet to be defined. To investigate these behaviors in thin film dielectric systems, PECVD SiON films that are known to store charge have been examined and compared to other dielectric films with varying degrees of conductivity. These comparisons were achieved by coupling a commercial nanoindentation system with a current and voltage source and an electrometer to produce both highly controlled contact stresses and accurate electrical measurements. The electrical behavior of thin film dielectrics as a function of stress, contact hold time and number of contact cycles will be discussed.

2:50 PM

Electrical Methods for Mechanical Testing of Interconnects: *Robert Keller*[1]; Nicholas Barbosa III[1]; Roy Geiss[1]; David Read[1]; Andrew Slifka[1]; [1]National Institute of Standards and Technology

A new approach to mechanical testing of dimensionally-constrained materials is presented. The testing methods are based on the principle of applying Joule heating to patterned interconnect specimens in a controlled manner, by use of low frequency, high current density a.c. electrical signals. The time scale is such that d.c. electromigration is precluded. Typical testing conditions include 100 Hz sinusoidal signals at a current density of 10 MA/cm^2. Thermal expansion mismatch between film and substrate then leads to thermal strains, which can be used as the basis for mechanical testing. We will demonstrate thermal fatigue testing on aluminum and copper lines, as well as strength measurements using extrapolations of well-known low-cycle fatigue concepts. The electrical test results are corroborated by microtensile testing. Deformation induced by thermal fatigue results in development of severe topography in non-passivated lines, as well as grain growth and re-orientation. Failure then takes place by open circuit.

3:05 PM

Determining Thin Film Properties by Nanoindentation of Film/Substrate Systems: *Seung Min Jane Han*[1]; William D. Nix[1]; [1]Stanford University

The Oliver & Pharr method for nanoindentation relies on an accurate determination of the contact area through a calibration process. However, it does not incorporate the effects of indentation shape (pile-up, sink-in) or the effects of elastic modulus mismatch that are typically present in film/substrate systems. Here we report a new methodology for calculating the true hardness of thin films on elastically mismatched substrates using an analytical treatment of the elastic indentation of a film/substrate with a conical indenter given by Yu et al. The method allows us to determine the contact radius and hardness from the measured contact stiffness and known elastic properties, even for indentation depths approaching the thickness of the film. The new method is applied to Al, W, and polymer thin films on various substrates to show that the true hardness of the thin films can be reliably determined using this method.

3:20 PM

Influence of Sample Offset Angle on Nanoindentation Test: Zhihui Xu[1]; *Xiaodong Li*[1]; [1]University of South Carolina

A key factor in measuring mechanical properties using nanoindentation is the accurate determination of real contact area. In nanoindentation analysis, the real contact area is derived from the unloading curve using a formula based on elastic solution of a rigid indenter perpendicularly penetrating a contact surface. In real test, such as indentations on samples with small dimension at micron/nano meter level, indentation is usually performed at a raw sample surface and it often happens that the indenter penetrate into the sample surface with certain offset angle. In this study, finite element simulation has been carried out to investigate the influence of sample offset angle on nanoindentation test. It is found that the increase in real contact area due to the sample offset angle cannot be accounted for with the current analysis technique of nanoindentation. This introduces significant error in the determination of mechanical properties, such as, hardness and elastic modulus.

3:35 PM Break

3:55 PM

Results of the NIST Nanoindentation Round Robin on Thin Film Copper on Silicon: *David Thomas Read*[1]; Robert R. Keller[1]; [1]National Institute of Standards and Technology

Nanoindentation is used in a variety of fields to measure material strength and stiffness. However, the standardization process for this new measurement method is still in progress. To test the ability of current measurement procedures to provide comparable results, a round robin was conducted. Invitations to participate were sent to over 100 laboratories. Two specimens, a copper film on a silicon substrate and an uncoated substrate, were distributed to 33 laboratories. The choice of measurement procedure was left to the performing organizations. To date 24 sets of results have been received, with more pending. The scatter is larger than expected. As of now, the standard deviation for the hardness of the copper film is 0.7 GPa, and for the substrate it is 1.3 GPa. The results will be examined to see if the scatter can be traced to particular aspects of the measurement procedures.

4:10 PM Invited

Nanoindentation of NiTi Shape Memory Alloys: *Kenneth Gall*[1]; Carl Frick[2]; [1]Georgia Institute of Technology; [2]University of Colorado

NiTi shape memory alloys have the ability to regain their shape after to deformation through a reversible thermo-elastic phase transformation. This study investigates the thermoelastic shear-driven martensitic transformation of NiTi at the nano-scale, and illustrates a connection between the martensite phase transformation in a nanometer-sized volume to the local material structure. Testing was performed on specimens machined from hot-rolled, polycrystalline Ti-50.9 at.%Ni. Small-scale mechanical behavior was probed by nanoindentation performed using a Berkovich indenter tip at a constant strain rate of 0.05. Both shape memory and pseudoelastic materials displayed reverse phase transformation upon unloading, specifically the shape memory NiTi showed discrete excursions in the load-depth response during both the loading and unloading. Furthermore, atomic force microscopy measurements subsequent to nanoindentation illustrated increasing deformation recovery upon heating as a function of decreasing indentation depth, for both the shape memory and pseudoelastic NiTi.

4:30 PM

Mechanical Properties of Pb-Free Solder Joints Associated with Intermetallics Growth Investigated Using Nanoindentation and OIM: *James P. Lucas*[1]; H. Rhee[1]; [1]Michigan State University

Mechanical properties of intermetallic compound (IMC) phases and bulk solder in Pb-free solder joints were assessed using nanoindentation testing (NIT) and orientation imaging (OIM). The elastic modulus and hardness were determined for IMC phases associated with in situ FeSn particle reinforced and mechanically-added Cu particle reinforced composite solder joints. IMC layers that formed around Cu particle reinforcement and at the Cu substrate/solder matrix interface were probed with NIT. Moduli and hardness values obtained by NIT revealed that Cu-rich Cu3Sn was noticeably higher than those of Cu6Sn5. Ag3Sn platelets that formed during reflow were also examined for eutectic Sn-Ag solder column joints. The indentation modulus of Ag3Sn platelets was significantly

lower than that of FeSn, SnCuNi, and CuSn IMCs. Indentation creep properties were assessed in localized microstructure regions of as-cast eutectic Sn-Ag solder. The stress exponent, n, associated with secondary creep differed widely and is relatable to microstructure features probed.

4:45 PM

Microbridge Tests on Buckled Thin Film Beams: *Tong-Yi Zhang*[1]; [1]Hong Kong University

We report here a microbridge testing method for buckled microbridge thin film beams due to residual compressive stress or/and residual moment in the beams. A theoretical formula based on the elastic beam theory is derived in closed form with the consideration of substrate deformation. Measuring the buckling profile of a microbridge beam without any original residual moment, one can evaluate Young's modulus and residual compressive stress of the beam. If there exists a residual moment in a multilayer microbridge beam, measuring the buckling profile and the slope of a load-deflection curve under small loads allows one to evaluate simultaneously the tension stiffness, the bending stiffness, the residual moment, and the residual force. Experimental results have verified the proposed microbridge testing method. The work is supported by an RGC grant from the Research Grants Council, HKSAR, China. Mr. B. Huang and Mr. X.S. Wang conducted the experiments.

5:00 PM

In Situ Neutron Measurement of Micromechanical Behavior of Materials under Applied Load at NRSF2: *Ke An*[1]; Cam R. Hubbard[1]; Hahn Choo[2]; William W. Bailey[1]; [1]Oak Ridge National Laboratory; [2]University of Tennessee

A neutron diffraction load frame has been constructed for the Second Generation Neutron Residual Stress mapping Facility (NRSF2) at ORNL's High Flux Isotope Reactor. The load frame is designed to study micromechanical behavior of materials under applied tensile, compressive or cyclic load and to characterize specimens while under load by using the NRSF2 mapping capabilities. Recently, in situ neutron measurements under different load conditions have been done: a) fast neutron measurements of Al 2024 and textured Al 5083 under continuous tensile load. Using the data summed from multiple detectors, we were able to collect neutron as fast as 3s/pattern. b) SiO2 particles in a compressive loading cell with either continuous or static load. c) SiC particulate reinforced Al2080 alloy composite measured with the SiC and Al hkls under position control. Details of the load frame design, the performance and those in situ results will be presented.

Effects of Water Vapor on High-Temperature Oxidation and Mechanical Behavior of Metallic and Ceramic Materials: Coatings and Ceramics

Sponsored by: The Minerals, Metals and Materials Society, ASM International, TMS Structural Materials Division, TMS/ASM: Corrosion and Environmental Effects Committee

Program Organizers: Bruce A. Pint, Oak Ridge National Laboratory; Peter Tortorelli, Oak Ridge National Laboratory; Karren More, Oak Ridge National Laboratory; Elizabeth Opila, NASA Glenn Research Center

Monday PM — Room: 213A
March 13, 2006 — Location: Henry B. Gonzalez Convention Ctr.

Session Chairs: Karren More, Oak Ridge National Laboratory; Elizabeth J. Opila, NASA Glenn Research Center

2:00 PM

Oxidation Behavior of Iron Aluminide Coatings in Water-Vapor Environment: *Ying Zhang*[1]; Bruce A. Pint[2]; Allen Haynes[2]; Ian G. Wright[2]; [1]Tennessee Technological University; [2]Oak Ridge National Laboratory

The long-term oxidation behavior of iron aluminide coatings, Fe_3Al or $(Fe,Ni)_3Al$, produced by a laboratory chemical vapor deposition (CVD) process on commercial ferritic steel Fe-9Cr-1Mo and austenitic stainless steel 304L, was studied in the temperature range of 700-800°C. For both substrates, the as-deposited coatings consisted of a relatively thin (20-25 μm) Al-rich outer layer and a thicker (150-275 μm) inner layer with less Al. The coating specimens were tested in air + 10 vol.% H_2O with 100-h cycle length for over 12,000h at 700°C and over 8,000h at 800°C, and they registered very low mass gains at both temperatures. While the aluminide coatings showed excellent oxidation performance at 700°C, spallation and re-formation of the oxide scale occurred at 800°C. In addition, the effect of N in the substrate alloy on the oxidation behavior of aluminide coatings was investigated via testing coated laboratory alloys with different N contents.

2:25 PM

Cyclic Oxidation and Mechanical Behavior of Slurry Aluminide Coatings for Steam Turbine Components: *Alina Agüero*[1]; Raul Muelas[1]; Marcos Gutierrez[1]; Rijk Van Vulpen[2]; Steve Osgerby[3]; L. Brown[3]; [1]Instituto Nacional de Técnica Aeroespacial; [2]KEMA; [3]National Physical Laboratory

The excellent steam oxidation resistance of iron aluminide coatings on ferritic steels at 650ºC has been demonstrated both by laboratory tests and field exposure. These coatings are formed by the application of an Al slurry followed by diffusion heat treatment at 700ºC for 10 hours. The resulting microstructure is mostly composed of Fe2Al5 on top of a much thinner FeAl layer. This coating exhibits perpendicular cracks and the results presented in this paper will show that these cracks are caused by a rapid cooling rate after heat treatment. However, these stress relieving cracks do not seem to have an effect in the mechanical properties of the substrate. The results of cyclic oxidation, creep resistance and TMF testing on these coatings will be presented.

2:50 PM

Effect of Water Vapor on Alumina-Forming Alloys and Coatings: *Bruce A. Pint*[1]; James Allen Haynes[1]; Ian G. Wright[1]; [1]Oak Ridge National Laboratory

Turbines fired with hydrogen or syngas from coal gasification will have significantly higher water vapor contents in the hot gas stream than natural-gas fired turbines. Previous work on alumina-forming MCrAl foils showed a consistent 10% reduction in the time to breakaway oxidation at 1100°C with the addition of 10% water vapor. Current work is examining the effect of up to 50% water vapor on the spallation resistance of cast alloys representing the major classes of Ni-base superalloy coatings (NiCrAlYHf, NiPt-40Al and NiPt-22Al+Hf) in cyclic testing at 1100°C. Initial work will be presented on coated superalloys in the same environments.

3:15 PM Break

3:30 PM

Role of Water Vapor in Affecting the Grain-Boundary Strength, Fracture, and Fatigue Properties of Alumina: *Jamie J. Kruzic*[1]; Rowland M. Cannon[2]; Robert O. Ritchie[3]; [1]Oregon State University; [2]Lawrence Berkeley National Laboratory; [3]University of California

Although weakened grain boundaries are essential for ceramics to achieve high strength and toughness, further degradation of their strength due to water vapor has been found to be detrimental to both the fracture and fatigue resistance. The role of moisture in affecting the fracture and fatigue-crack growth resistance of a 99.5% pure polycrystalline alumina has been examined in moist and dry environments at ambient temperature. In addition to the expected higher intrinsic toughness, it was found that the R-curves initially rise more steeply in dry environments. Similarly, improved fatigue resistance was found in dry environments and for both this is attributed to changes in the nature of the bridging, with uncracked-ligament bridges playing a larger role in dry atmospheres, while frictional bridges are predominant in moist air. Such behavior is also expected to be relevant at elevated temperatures since the chemical reaction at the crack tip will be further promoted.

3:55 PM

Evaluation of NZP Ceramic Variants for EBC Applications: *Ramachandran Nageswaran*[1]; Karren More[2]; [1]SMAHT Ceramics, Inc.; [2]Oak Ridge National Laboratory

Silicon carbide (SiC) and silicon nitride (Si3N4) based monolithic or composite turbine engine components require an environmental barrier coating ("EBC") to prevent water vapor attack of the protective silica

layer and associated material recession during high temperature operation. The state-of-the-art EBC, which is based on mullite and BSAS (barium strontium alumino-silicate), provides good environmental protection for the Si-based ceramics for up to several hundred hours at 1250°C. Nevertheless, further enhancement of the EBC performance is critical for reliable operation of advanced turbine engines. A few compositional variants from the [NZP] family of ceramics, such as BZP (Barium Zirconium Phosphosilicate), have attractive properties such as low moisture sensitivity, high thermal cycling stability and low thermal conductivity. Recent high water-vapor pressure rig testing of BZPs at 1200°C up to 1000 hrs., in the Kaiser Rig, yielded promising data. Results from this EBC development effort are presented in this paper.

4:20 PM

Stress-Dependent Molecular Pathways of Silica-Water Reaction: *Ting Zhu*[1]; Ju Li[2]; Xi Lin[3]; Sidney Yip[3]; [1]Georgia Institute of Technology; [2]Ohio State University; [3]Massachusetts Institute of Technology

We study stress-corrosion of silica by water through exploring the stress-dependent molecular pathways of silica-water reaction. An ordered silica nanorod with clearly defined nominal tensile stress is constructed to model a structural unit of the stressed crack tip. Three competing hydrolysis reaction pathways are identified, each involving a distinct initiation step. Water dissociation, molecular chemisorption, and direct siloxane bond rupture dominate at low, intermediate, and high stress levels, respectively. A linear stress dependence in the thermodynamic driving force, not commonly considered in the criterion of brittle fracture initiation, is shown to originate from surface relaxation associated with bond rupture. This effect is particularly important in determining the Griffith condition of crack extension for nano-sized systems when spatial accommodation of foreign molecules is involved in the process of bond breaking.

Fatigue and Fracture of Traditional and Advanced Materials: A Symposium in Honor of Art McEvily's 80th Birthday: Fatigue and Fracture II

Sponsored by: The Minerals, Metals and Materials Society, TMS Structural Materials Division, TMS/ASM: Mechanical Behavior of Materials Committee

Program Organizers: Leon L. Shaw, University of Connecticut; James M. Larsen, U.S. Air Force; Peter K. Liaw, University of Tennessee; Masahiro Endo, Fukuoka University

Monday PM — Room: 216
March 13, 2006 — Location: Henry B. Gonzalez Convention Ctr.

Session Chairs: Hael Mughrabi, Universität Erlangen-Nuernberg; Paul C. Paris, Washington University in St. Louis

2:00 PM Invited

Damage Mechanisms of Cast Al-Si-Mg-Alloys under Superimposed Thermal-Mechanical- and High-Cycle-Fatigue Loading: *Detlef Loehe*[1]; Tilmann Beck[1]; Jochen Luft[1]; Ingo Henne[1]; [1]Universität Karlsruhe

In order to analyze the synergy of damage caused by the low frequency thermal and the high-frequency mechanical loading and to get quantitative fatigue life data of cast aluminium alloys, superimposed thermal-mechanical fatigue (TMF)/high-cycle fatigue (HCF) tests at the cylinder head alloys AlSi7Mg, AlSi5Cu4 and AlSi10Mg were conducted in total strain control. Extensive metallographic and SEM studies of the crack initiation and propagation process were conducted. Under TMF as well as under TMF/HCF loading, cracks are always initiated at the interface between eutectic Si-particles and α-Al matrix. Under pure TMF conditions, the cracks propagate solely along the eutectic regions, whereas with increasing superimposed HCF loading crack propagation along slip bands within the primary α-Al crystals becomes more dominant. Based on the damage parameters developed, a method for lifetime estimation under superimposed TMF/HCF loading on the crack propagation process is developed.

2:25 PM Invited

Parameters and Key Trends Effecting Fatigue Crack Growth - A Tribute to Professor Arthur J. McEvily's Contributions: *Diana A. Lados*[1]; Paul C. Paris[1]; [1]Washington University in St. Louis

The early 1950s led to high performance aluminum skinned aircraft for which metal fatigue and fatigue crack growth became extremely important considerations. Virtually, no significant range of data on fatigue crack growth existed prior to McEvily's work[1], and controlling parameters were left to be further developed. His pioneering work allowed others to resolve some of the critical issues, and yet a few still remain open even today. This discussion will trace historical milestones in the field, as well as some more recent investigations, with the intention of exposing the major trends. Finally, a new methodology for analyzing fatigue crack growth load-displacement records to determine "effective stress intensity factor ranges", the major mechanical cause of crack growth, will be discussed. [1]A. J. McEvily Jr. and W. Illg; The Rate of Fatigue Crack Propagation in Two Aluminum Alloys, NACA (now NASA), TN 4394, 1958.

2:50 PM Invited

Mechanisms of the Early Fatigue Damage in Crystalline Materials: *Jaroslav Polak*[1]; [1]Institute of Physics of Materials ASCR

Cyclic loading of crystalline materials introduces damage, which is difficult to quantify. Recent applications of the transmission electron microscopy, high resolution scanning electron microscopy, atomic force microscopy and electron back scattering to study the early damage in polycrystalline materials will be reviewed and documented. The experimental findings will be used to identify the principal mechanisms leading to fatigue damage. Dislocation rearrangement resulting in cyclic strain localization, the surface relief evolution producing the extrusions and intrusions and ending in crack initiation will be reported and analyzed in reference to recent theories of fatigue crack nucleation. The growth of initiated cracks under constant plastic strain amplitude loading will be reviewed. The growth kinetics and the parameters of the short crack growth law will be compared with the fatigue life curves determined under identical loading conditions. This results in interpretation of the Manson-Coffin law in terms of short crack growth.

3:15 PM Invited

The Use of Modeling and Experiment to Understand "Dwell Fatigue" in Ti Alloys: *James C. Williams*[1]; Somnath Ghosh[1]; Michael J. Mills[1]; Stan Rokhlin[1]; Vikas Sinha[1]; [1]Ohio State University

There is a fatigue failure mode in high temperature Ti alloys known as Dwell Fatigue. This mode is characterized by a major reduction in fatigue life when the material is subjected to a loading pattern where the load is held at maximum value for a dwell period. Moreover, this failure mode is typified by subsurface crack initiation. Because of its importance, the phenomenology of dwell fatigue is well defined. However, the fundamental reasons for its occurrence are not well understood. This talk will describe the phenomenology of dwell fatigue, followed by results of a multi-year, interdisciplinary study of dwell fatigue in Ti-6Al-2Sn-4Zr-2Mo (+Si). We have used solid mechanics modeling, detailed characterization methods and high resolution acoustic microscopy to study this mode of failure. The current qualitative state of understanding and future directions to develop a quantitative understanding will be described.

3:40 PM Break

3:55 PM Invited

Microstructural Roles in Thermal-Mechanical and Isothermal Low Cycle Fatigues of a Single Crystal Ni-Base Superalloy: *Masakazu Okazaki*[1]; Motoki Sakaguchi[1]; [1]Nagaoka University of Technology

Behavior of themal-mechanical fatigue (TMF) failure of CMSX-4 was studied, compared with that of isothermal low-cycle fatigue (ILCF). Strain-controlled TMF and ILCF tests were carried out under various test conditions, where the experimental variables were strain rates, strain ratio, test temperature and the range, and strain/temperature phase angle. It was shown from the experiments that the TMF and LCF failures occurred, associated with some noteworthy characteristics which were rarely seen in the traditional pollycrystalline heat-resistant alloys. They could be explained inadequately, on the basis of the macroscopic parameters and the historical failure criteria. A new micromechanics model is proposed to predict the TMF and LCF lives, based on the Eshelby's theory. In the

model the microstructural factors are represented by both the difference of mechanical properties between the gamma matrix and the cuboidal gamma-prime precipitates, and the lattice misfit between them which induces internal stress.

4:20 PM Invited
Cyclic Deformation Behavior of Steels and Light Metal Alloys: *Dietmar Eifler*[1]; Frank Walther[1]; [1]University of Kaiserslautern

Detailed knowledge about the cyclic deformation behaviour of metallic materials is a indispensable requirement for the comprehensive understanding of fatigue processes and a reliable lifetime prediction of cyclically loaded components. Besides various steels (e.g. SAE 4140, railway wheel steels) aluminium, magnesium and titanium alloys were investigated in stress- and strain-controlled fatigue experiments. In addition to mechanical stress-strain hysteresis measurements, changes of the specimen temperature and the electrical resistance were regarded. The deformation-induced martensite formation of metastable austenite was detected in-situ with a FerriteScope. As advanced measuring technique Giant Magneto Resistance (GMR) sensors were used. The results of all measurements depend on microstructural changes due to plastic deformation processes and therefore show a clear interaction with the actual fatigue state. The measured values were presented in cyclic deformation, Morrow and Manson/Coffin curves for lifetime prediction. S,N-curves were described according to Basquin. The microstructures were characterized by scanning and transmission electron microscopy.

4:45 PM Invited
Effect of Environment on Thermomechanical Fatigue Life: *Hans-Juergen Christ*[1]; [1]Institut für Werkstofftechnik, Universität Siegen

Results of various studies on the thermomechanical fatigue (TMF) behaviour of metallic engineering materials performed in the research group of the author are presented showing the effect of laboratory air as compared to high vacuum. In order to illustrate the variety of possible effects, three different materials are considered. An austenitic stainless steel is an example for rather small environmental effects on TMF lifetime. At high maximum temperatures applied in the TMF cycle, creep damage prevails. Hence, in-phase (IP) testing is more detrimental than out-of-phase (OP) loading. Vacuum shifts the crack initiation site from the interior to the surface leading to similar lives in IP and OP. The high-temperature titanium alloy IMI834 suffers from hydrogen embrittlement at moderate temperatures and oxygen uptake at high temperatures. Consequently, the environmental influence on life is pronounced. TiAl-based intermetallic alloys show high environmental susceptibility, which is promoted by the strong ductile-to-brittle transition.

General Abstracts: Electronic, Magnetic, and Photonic Materials Division: Session II

Sponsored by: The Minerals, Metals and Materials Society, TMS Electronic, Magnetic, and Photonic Materials Division, TMS: Alloy Phases Committee, TMS: Biomaterials Committee, TMS: Chemistry and Physics of Materials Committee, TMS: Electronic Materials Committee, TMS: Electronic Packaging and Interconnection Materials Committee, TMS: Nanomaterials Committee, TMS: Superconducting and Magnetic Materials Committee, TMS: Thin Films and Interfaces Committee
Program Organizers: Sung K. Kang, IBM Corporation; Long Qing Chen, Pennsylvania State University

Monday PM — Room: 211
March 13, 2006 — Location: Henry B. Gonzalez Convention Ctr.

Session Chair: Sung K. Kang, IBM Corporation

2:00 PM Introductory Comments

2:05 PM
Fabrication of Oxide Superconducting Thin Films Using Colloids of Nano-Particles as Precursor: *Vamsee K. Chintamaneni*[1]; Jinhua Su[1]; Pratik Joshi[1]; Sharmila M. Mukhopadhyay[1]; Ramchander Revuru[2]; Troy Pyles[2]; Suvankar Sengupta[2]; [1]Wright State University; [2]Metamateria Partners LLC

The most popular non-vacuum method of creating thin film oxide superconductors, YBa2Cu3O7-x (YBCO) is the Metal Organic Deposition technique using Tri-fluroacetate solution (MOD-TFA method). The main draw backs for this process are: (i) long process time, and (ii) porosity in the final film. In this study, an alternative method was used to fabricate lower porosity films at a significantly faster rate. The precursor used is a colloidal suspension of Y-Ba-Cu-O nanoparticles in an organic solvent. Precursor films were deposited on (100) LaAlO3 by spin coating and heat treated in two stage annealing process to obtain final films. The microstructure, texture, critical temperature (Tc), critical current density (Jc) and chemistry of these films will be compared to YBCO films prepared by other processes (MOD-TFA, as well as well characterized vacuum techniques), and the different mechanisms of film growth discussed.

2:30 PM
Impact of Interface Chemistry on the Occurrence of Anomalous Near-Threshold Debond Growth Rate Behavior in Thin-Film Structures: *Bree M. Sharratt*[1]; Reinhold H. Dauskardt[1]; [1]Stanford University

The integrity of thin film structures is often limited by interface adhesion. Polymer/inorganic interfaces are especially vulnerable and understanding the relationship between loading, environment and interface chemistry is crucial. We report the susceptibility of a model bisphenol F/SiN_x interface to subcritical debonding. An anomalous near-threshold region developed where growth rates showed only slight dependence on the applied load but were accelerated with increasing temperature and relative humidity. A new stress-dependent transport model is presented that predicts growth rates in this region. By modifying both the epoxy layer and the interface using adhesion promoting molecules, the effect of interface chemistry was systematically examined. We discuss the effects of blended adhesion promoters on the mechanical properties of the bisphenol F film and relate these to variances in adhesion and subcritical debonding behavior. Finally, with effects on the occurrence of the anomalous near-threshold region highlighted, differences between blended and spun-on specimens are presented.

2:55 PM
Integration of Electroplating and Electropolishing of Cu Damascene Process: *Sue-Hong Liu*[1]; Chih Chen[1]; Jia-Min Shieh[2]; Bau-Tong Dai[2]; Shih-Song Cheng[3]; Karl Hensen[3]; [1]National Chiao-Tung University; [2]National Nano Device Laboratories; [3]BASF Electronic Material Ltd.

An effective technology containing two functions of Cu film depositing and polishing in one-step electrochemical process in one tank has been developed, and it will save many risks and cost at the back end of the interconnect fabrication. A promising method, which can be called Cu dual-mode electroplating, integrates the process of electroplating and electropolishing in one tank by alternating the program of controlled computer and exchanging the electrode during electrochemical process. Furthermore, the novel electrolyte in this study consists of phosphoric acid and other organic additives with appropriate concentration and standard Cu electroplating solutions. The already tested conditions were the pulse-time and cycles, various concentrations of organic additives, phosphoric acid. Finally, a high planar Cu surface and profile, Cu films with high filling capability in small trench width and step-height reduction in various pattern sizes (1-50 μm) were obtained after Cu Dual-Mode plating.

3:20 PM
Photocatalytic Activity and Control of Grain Size in Tio2 Nanocomposite with Nanometer-Sized Paticles by Mechanical Alloying and Heat Treatment: *Dong Hyun Kim*[1]; Ha Sung Park[1]; Jae Han Jho[1]; Sun-Jae Kim[2]; Kyung Sub Lee[1]; [1]Hanyang University; [2]Sejong University

Nanocomposite of Ni-doped rutile TiO2 and NiTiO3 were synthesized by mechanical alloying and heat treatment. Nanocomposite showed higher photocatalytic activity than that of pure anatase TiO2 and commercial P-25 for decomposition of benzene. And the absorption threshold of the nanocomposite TiO2 moved to a longer wavelength. The new absorption was believed to be induced by the trapping band gap between the valence and conduction bands of nanocomposite TiO2. Formation of NiTiO3 in Ni doped TiO2 by heat treatment was found to control the grain growth of

nano size TiO2 and to enhance the high temperature thermal stability. Nanocomposite TiO2 powders had a grain size in the range 10-20 nm.

3:45 PM Break

4:15 PM

The Effects of Deformation on the Magnetic Behavior of Stoichiometric Ni_3Al: Q. Zeng[1]; *Ian Baker*[1]; [1]Dartmouth College

Strain-induced ferromagnetism (SIF) has been observed in a number of intermetallic compounds containing magnetic moment-bearing elements. This phenomenon has been quantitatively modeled in cold-rolled FeAl, using the local environment theory, based on the idea that the ferromagnetism arises from the local disorder in APB tubes. While compounds such as Fe_2AlMn and Co_3Ti show SIF, the reverse effect has been observed in cold-rolled stoichiometric Ni_3Al single crystals. This presentation describes investigations into the effects of disorder on the magnetic magnetic behavior of both cold-rolled, and ball-milled and annealed stoichiometric Ni_3Al via x-ray diffraction, differential scanning calorimetry, and magnetic and thermal-magnetic studies. Research sponsored by NIST grant 60NANB2D0120.

4:40 PM

Magneto-Optic Lens Using Ferrofluids: Jayachandran Nagarajan[1]; *Namasivayam Murugesan*[1]; [1]Velammal Engineering College

γ-Fe2O3, water based ferrofluid (maghemite) has a good transmittance. At a low magnetic volume fraction it is possible to obtain good magneto-optic effect and transmittance. Without any applied field ferrofluids are isotropic. But when a magnetic field is applied ferrofluids acquire an optical anisotropy. Two cases are possible: *Faraday's rotation of plane polarized light when magnetic field is parallel to the light beam. *Anisotropy is linear in perpendicular configuration. If ferrofluid is placed in a cylinder acting as electromagnet producing lines of flux in direction of light, due to attraction of flux linear, more fluid is attracted near cylinder wall. This pattern acts as a lens and can be varied depending upon the field of electromagnet and produce auto focal lens. With sol-gel doped ferrofluid, higher transmittance is obtained. Uses: *In focusing of laser with wavelet filter. *To develop artificial human eye lens.

5:05 PM

CBED Measurements of Lattice Strain in Strained Silicon – Relaxation, HOLZ Line Splitting and Overall Reliability: *David R. Diercks*[1]; Michael Kaufman[1]; [1]University of North Texas

The role of lattice strain is important in next-generation CMOS devices. Convergent beam electron diffraction is potentially well suited for such analyses. By comparing the higher order Laue zone lines in a strained region to those from unstrained material, the nature of the strain can be determined. To date, these measurements are made at large angles relative to the <011> cross-section normal. In this study, to achieve better lateral resolution, zones at smaller tilts such as <056> have been examined using thin Si-15%Ge samples on silicon. It is shown that certain HOLZ lines split near the interface; from this, it is concluded that considerable relaxation occurs during the preparation of TEM specimens resulting in strain behavior not indicative of the bulk strain. The variation in splitting as a function of distance from the interface, sample thickness and specimen geometry is described and related to a physical model of the relaxation.

General Abstracts: Extraction and Processing Division: Copper/Nickel

Sponsored by: The Minerals, Metals and Materials Society, TMS Extraction and Processing Division, TMS: Aqueous Processing Committee, TMS: Copper and Nickel and Cobalt Committee, TMS: Lead and Zinc Committee, TMS: Precious Metals Committee, TMS: Process Fundamentals Committee, TMS: Process Modeling Analysis and Control Committee, TMS: Pyrometallurgy Committee, TMS: Recycling Committee, TMS: Waste Treatment and Minimization Committee, TMS: Materials Characterization Committee
Program Organizers: Thomas P. Battle, DuPont Company; Michael L. Free, University of Utah; Boyd R. Davis, Kingston Process Metallurgy

Monday PM
March 13, 2006

Room: 207A
Location: Henry B. Gonzalez Convention Ctr.

Session Chair: Mark E. Schlesinger, University of Missouri

2:00 PM

Neutralization of Smelter Gases with Limestone in a Countercurrent Multiple Fluidized Bed System: *Igor Wilkomirsky*[1]; F. Parada[1]; R. Parra[1]; [1]University of Concepcion

A novel process to neutralize SO2 from concentrated copper smelter off gases is being developed. The process uses a three-stages fluidized beds that allows to reacts the SO2 from the ascending gases with a countercurrent flow of fluidized limestone. The overall reaction forms anhydrous sulphate and CO2, generating a heat surplus of –77.35 kcal/mol of SO2. The reaction is very fast over 750°C, capturing over 99% of the SO2 at 800°C. For a gas with 8%SO2 the off gases contained 0.07% SO2. The capture is equally efficient for diluted gases (0.5%) and concentrated gases (12%).

2:25 PM

Decomposition Behaviour of Metallic Sulphates and Copper Flash Smelting Flue Dust: *Elli Vilhelmiina Nurminen*[1]; [1]Helsinki University of Technology

Thermodynamics of metallic sulphate decomposition reactions were studied through thermodynamical calculations and thermogravimetric methods including evolved gas analysis. The decomposition temperatures and mechanisms were determined for cupric sulphate, ferric sulphate and also for industrial flue dust from a copper flash smelting process. The aim was to determine the thermodynamic conditions for sulphate decomposition and to estimate whether the reactions are likely to take place in the flash smelting process heat recovery equipment. The information is essential in CFD-modelling of the reactions taking place in the boiler and for optimising the process.

2:50 PM

Intensification and Increase of Smelting Furnace Productivity Thorough On-Line Optimization and Automation of Pyrometallurgical Processes: *Florian Kongoli*[1]; I. McBow[1]; Robert D. Budd[1]; S. Llubani[1]; [1]FLOGEN Technologies Inc

Process intensification and the increasing the productivity of the smelting furnaces is an important issue for various pyrometallurgical processes. That is closely related to several factors from decreasing the number of smelting problems and accidental shutdowns to the optimization and automation of these processes. In this paper, the authors discuss their recent work in effectively controlling acute industrial furnace problems such as magnetite build-up and accretions, eliminating unnecessary slag foaming, decreasing slag losses etc as well as the intensification, optimization and automation of these processes through a unique process physical modeling that correctly simulate the industrial furnace processes and avoid guessing and uncertainties. The advantages of this new approach have been discussed.

3:15 PM

Dissolution Behavior of Solid Cu2O in Na2O-B2O3-Based Slags: *Weol Dong Cho*[1]; Jei-Pil Wang[1]; [1]University of Utah

The dissolution behavior of copper oxide (Cu2O) in Na2O-B2O3-based slags has been studied in terms of kinetics and equilibrium solubility in

the temperature range of 900-1100°C. The spherical single phase copper oxide powers were prepared by the oxidation of pure copper powders in a fluidized bed at high temperatures. The oxide particles are added directly into the molten slags and the variation of the particle size with time was determined using optical and electron microscopes to get dissolution rate. The effect of temperature and slag composition on the rate of dissolution and the equilibrium solubility of the solid copper oxide was determined for the slag system. Based on the kinetic data and the properties of the slags, the dissolution mechanism has been discussed.

3:40 PM

Reduction of Nickel Oxide from Liquid Slags with Carbon and Silicon: *Antonio Romero-Serrano*[1]; Patricia Martínez-Nicolas[1]; Samuel González-López[1]; Miguel Angeles-Hernández[1]; [1]National Polytechnic Institute

Nickel and ferronickel are some of the major components in the production of special alloys; however, the energy consumption for their production greatly increases their price. A cheaper option could be to use NiO and a reducing element. This work presents experimental and theoretical analysis to estimate the effect of slag basicity and amount of reducing agents on the NiO reduction from the slag which interacted with molten steel at 1600°C in an EAF. The slag system contained CaO-SiO2-CaF2-NiO together with a reducing agent, ferrosilicon or carbon. The NiO content in the slag was 25 mass%. The amounts of the reducing agents were 1 to 4 times the stoichiometric mass to reduce NiO. The CaO/SiO2 ratio was 1.5 and 2.5. The kinetics of the process was very fast since after 5 min the maximum nickel yield was obtained. The slag basicity had a negligible effect on the NiO reduction.

4:05 PM Break

4:25 PM

Energy Requirements in Nickeliferous Laterite Treatment: Emmanuel N. Zevgolis[1]; *Charalabos Zografidis*[1]; John Gaitanos[2]; Ismine Polyxeni Kostika[1]; Iliana Halikia[1]; [1]National Technical University of Athens; [2]General Mining and Metallurgical Company S.A. Larco

Treatment energy for a nickeliferous laterite ore by the rotary kiln - electric furnace process is investigated. From this work it comes that thermal energy is about 65% of the total energy needed and the rest is electrical. Also, 56.2% of thermal energy input in the roasting step (that is, the energy of all combustibles fed into the rotary kilns) is used for preheating, 18% for prereduction and the rest (25.8%) corresponds to energy of remaining carbon in the kiln products (i.e., calcine, dust and coatings). Additionally, 57.1% of total carbon entering the system (Ctot) is used for combustion, 38.6% for reduction and the rest (4.3%) remains unburnt. Exploitation of energy from gases of both furnaces, as well as the higher possible reduction degree, the optimum temperature of the calcine and also elimination of the excess air in the rotary kilns, improve significantly energy balance and economics of the process.

4:50 PM

Control of Foaming Phenomena during Copper Blow in Copper P-S Converter: *Pengfu Tan*[1]; Pierre Vix[1]; [1]Xstrata Copper

Xstrata Copper at Mount Isa in Australia has operated copper Isasmelt furnace and 4 P-S converters. The phenomena of foaming occur in above 10% of converter operations. A thermodynamic model of copper P-S converter has been developed to simulate copper blow. The model predicts the chemistry of copper skims during copper blow. The effects of oxygen potential charge of dirty materials, slag carry over, and temperature on the foaming and viscosity of copper skims have been discussed. Some improvements of the industrial operations have been presented.

General Abstracts: Extraction and Processing Division: Hydrometallurgy

Sponsored by: The Minerals, Metals and Materials Society, TMS Extraction and Processing Division, TMS: Aqueous Processing Committee, TMS: Copper and Nickel and Cobalt Committee, TMS: Lead and Zinc Committee, TMS: Precious Metals Committee, TMS: Process Fundamentals Committee, TMS: Process Modeling Analysis and Control Committee, TMS: Pyrometallurgy Committee, TMS: Recycling Committee, TMS: Waste Treatment and Minimization Committee, TMS: Materials Characterization Committee
Program Organizers: Thomas P. Battle, DuPont Company; Michael L. Free, University of Utah; Boyd R. Davis, Kingston Process Metallurgy

Monday PM — Room: 202B
March 13, 2006 — Location: Henry B. Gonzalez Convention Ctr.

Session Chair: Michael L. Free, University of Utah

2:00 PM

Effect of Normality, Temperature and Time on the Tungsten Losses in the Residue Separated from Diluted Scheelite-Slurry-in-NaOH after Digestion: *Raj Pal Singh*[1]; [1]Osram Sylvania Inc

Due to high concentration of NaOH in the digested slurry after scheelite digestion, it is diluted to about 4N before filtration to separate sodium tungstate solution from the sludge (residue). However, in practice there may be deviations in the normality of NaOH present in the slurry. There may also be variations in the temperature of the slurry and filtration time. Slight variations in these parameters could cause tungsten losses in the sludge via the back reaction: $Ca(OH)_2 + Na_2WO_4 \longrightarrow CaWO_4 + 2NaOH$ This paper pertains to the effect of normality, temperature and time on the tungsten losses in the sludge that is separated from "diluted-scheelite-slurry-in-NaOH" via filtration. Results indicated that tungsten losses in the filtered residue (sludge) were quite significant when the slurry temperature was kept at 70°C or higher. The effect of high temperature was less significant at the slurry normality of 3.6 or higher. Combination of low slurry normality (<3.6) and high temperature (>60C) resulted into large W-losses in the sludge.

2:25 PM

Hydrometallurgical Processing of Mechanically Activated Zircon Concentrate: Ashraf Amer[1]; *Salah Megahed*[1]; [1]Alexandria University

Among the minerale of the black sand of Egypt is zircon which is found in an economic value (7.3%). These sands are found along the Mediterranean coast of Nile Delta. The present investigation aimed at studying the effect of mechanical treatment on the extraction of zirconium from Egyptian zircon concentrate, the effect of temperate grinding time, sodium hydroxide concentration and leaching time on the extraction of zirconium as well as the kinetics of the leaching process have been studied. Experimental leaching of zircon concentrate has shown that the zirconium extraction (90%) can be reached after mechanical treatment of the studied zircon concentrate, followed by alkali leaching at 190 C in an autoclave.

2:50 PM

Study on Recovering Iron-Bearing Minerals from a Nickel Metallurgical Residue by Selective Flocculation-Magnetic Separation: *Haigang Dong*[1]; Yufeng Guo[1]; Tao Jiang[1]; Guanghui Li[1]; [1]Central South University

Mineralogy and phsico-chemical performance of nickel metallurgical residue and recovery of iron-bearing minerals by flocculation-magnetic separation were studied. The results were as follows: The nickel metallurgical residue is fine mineral and content reachs 85.4%. Iron-bearing minerals are chiefly magnetite and ferruginous vitreum which exist in -0.045mm mainly. Magnetite accounts for 31.7% of total iron which is in existence of monomer. A few magnetite distribute in ferruginous vitreum. Ferruginous vitreum with stronger magnetism and low-iron accounts for 39.9% of total iron, which is a multicomponent amorphous state substance. Addition of iron flocculant increased granularity and magnetic force of fine iron particles and improve iron grade and recovery rate. Iron

grade of 56.08% and recovery rate of 81.72% were obtained by flocculation-magnetic separation under conditions of oleic acid 0.8kg/t, sodium carbonate2kg/t and magnetic density 2500Gs.

3:15 PM Break

3:30 PM
The Technological Characteristics of Blended Nkalaha and Nsu Clays: *Ndubuisi Edennaya Idenyi*[1]; Sampson I. Neife[2]; Stanley O. Agha[1]; [1]Ebonyi State University; [2]Enugu State University of Science and Technology

The effects of compositions and firing temperatures on the physico-mechanical properties of blended Nsu fireclay and Nkalaha redbrick clay both in the southestern states of Imo and Ebonyi in Nigeria have been investigated. The clay samples were compounded according to the following ratios; 10:90, 20:80, 30:70, 40:60, 50:50, 60:40, 70:30, 80:20, and 90:10 in the order Nsu: Nkalaha respectively, and test samples made and fired at 900°C, 1000°C, 1100°C and 1200°C. The properties investigated wer the modulus of rupture (green, dry, and fired), apparent porosity, shrinkage (wet, dry, fired and total), apparent density, bulk density, and water absorption. From the results obtained, the blends were found to have a maximum service temperature of 1100°C; with the 30:70 blends presenting the best characteristics. A conclusion is drawn to the effect that the clay blends could be adapted for the production of ceramic earthenware, electrical porcelain pin insulators, in cement making and for lining of metal melting furnaces where temperature requirements are less severe.

3:55 PM
A Clean Method Applying Anion-Exchange Separation and Membrane-Electrolysis to Regenerate Fe-Zn-HCl Spent Pickling Liquors: *Gabor Csicsovszki*[1]; Tamas Kekesi[1]; Tamas I. Torok[1]; [1]University of Miskolc

We have developed a novel method - at the laboratory scale - comprising an ion-exchange separation and a membrane-electrolysis step for the purpose of zero-waste regeneration of spent HCl pickling liquors originating from hot-dip galvanizing of common steels. It is aimed at the parallel regeneration of HCl and iron. Experiments revealed that iron can be electrodeposited at high current efficiencies by maintaining the following conditions: 0.04-0.08 M HCl, 500-1000 A/m^2, 20°C and stationary electrolyte in a conventional cell. Zinc in the solution did not disturb the deposition of iron, however it contaminated the product and it poisons the anion-exchange membrane required to tackle acidity during electrolysis. For a preliminary separation, anion-exchange tests were carried out to produce pure iron solutions. Beyond the equilibrium studies, column experiments were carried out showing that low flow rates of the loading solution and the ~1.5 M HCl eluent are essential for separation.

4:20 PM
Comprehensive Utilization of Zinc Leach Residues by Flotation - Reduction Roasting - Magnetic Separation Process: *Tao Jiang*[1]; Yuanbo Zhang[1]; Zhucheng Huang[1]; Guanghui Li[1]; Yongbin Yang[1]; Yufeng Guo[1]; Bin Xu[1]; [1]Central South University

Zinc leach residues produced by hydrometallurgical zinc plant contain many valuable elements (zinc, gallium, germanium, silver, etc), while they have not been utilized effectively hitherto. In this paper, a new process of flotation-reduction roasting-magnetic separation to recover them is developed. The results show that, using Na_2S as conditioner, ammonium dibutyl dithiophosphate and SN-9 (assistant collector) as combined collector and terpenic oil as frother, if zinc leach residues with 523 g/t silver are floated at pH = 5.0, over 80% silver is recovered from the residues. When the flotation tailings are subjected to reduction roasting at 1100°C for 2 h, volatilization rates of zinc, lead and indium are over 96%. After roasted products are treated by wet-grinding and magnetic separation, recovery of gallium and germanium can reach 93-95%. The new process brings out no secondary pollution.

Hume Rothery Symposium: Multi-Component Alloy Thermodynamics: Alloy Physics

Sponsored by: The Minerals, Metals and Materials Society, TMS Electronic, Magnetic, and Photonic Materials Division, TMS: Alloy Phases Committee
Program Organizers: Y. Austin Chang, University of Wisconsin; Rainer Schmid-Fetzer, Clausthal University of Technology; Patrice E. A. Turchi, Lawrence Livermore National Laboratory

Monday PM
March 13, 2006
Room: 202A
Location: Henry B. Gonzalez Convention Ctr.

Session Chairs: Y. Austin Chang, University of Wisconsin; Patrice E. A. Turchi, Lawrence Livermore National Laboratory

2:00 PM Introductory Comments

2:05 PM Invited
Entropies of Formation and Mixing in Alloys: *William Alan Oates*[1]; [1]University of Salford

Entropy often plays a major role in determining the relative stability of phases in a system at high temperatures. Some examples of where this role is particularly apparent will be presented. Methods which may be used for estimating the magnitude of the contributions to formation/mixing entropies will then be discussed. Special emphasis will be placed on models which can be of value in the calculation of formation/mixing entropies for real multi-component alloys and which are, therefore, of value in the calculation of phase diagrams for multi-component, multi-phase systems. The value of the cluster/site approximation for describing the configurational contributions in such systems will be emphasized and some recent developments in its application will be presented. Some consideration will also be given to methods suitable for the estimation of the magnitude of other contributions to formation/mixing entropies.

2:55 PM Invited
Application of First-Principles Methods in the Modeling of Multicomponent Alloys: Axel Van De Walle[1]; Gautam Ghosh[1]; *Mark D. Asta*[1]; [1]Northwestern University

This talk will review recent applications of first-principles methods in the modeling of multicomponent alloy phase stability. Our overall strategy involves the use of first-principles methods to augment thermodynamic databases with the aim of increasing the predictive capability of more traditional computational-thermodynamic models. In the Al-Ti-Zn system first-principles methods combined with a sublattice cluster-expansion formalism are used to find the optimal concentrations for stabilizing ternary two-phase fcc/L12 microstructures. For Al-Hf-Nb we demonstrate how first-principles calculations of the energies of stable and virtual compounds and solid solutions can facilitate CALPHAD modeling of ternary isothermal sections, with applications to the design of a high-temperature alloy. Finally, we discuss recent additions to the Alloy Theoretic Automated Toolkit (ATAT) which allow first-principles ternary cluster expansions to be formulated for use in deriving ternary ground-state compounds and thermodynamic properties. Applications of this methodology in Ni and Fe based alloys will be shown.

3:25 PM Break

3:45 PM Invited
Atomistic Modeling of Multicomponent Systems with Quantum Approximate Methods: *Guillermo Bozzolo*[1]; [1]Ohio Aerospace Institute

The need to accelerate materials design programs based on economical and efficient modeling techniques provides the framework for the introduction of approximations in otherwise rigorous theoretical schemes. Several quantum approximate methods have been introduced through the years, bringing new opportunities for the efficient understanding of complex multicomponent alloys at the atomic level. As a promising example of the role that these methods might have in the development of complex systems, in this work we discuss the BFS method for alloys and its application to a variety of multicomponent systems for a detailed analysis of their defect and phase structure and their properties. Examples include

the study of the phase structure of new Ru-rich Ni-base superalloys, the role of multiple alloying additions in high temperature intermetallic alloys, and interfacial phenomena in nuclear materials, highlighting the benefits that can be obtained from introducing simple modeling techniques to the investigation of complex systems.

4:15 PM Invited
Theoretical Investigation of Phase Equilibria for a Metal-Hydrogen Alloy: *Tetsuo Mohri*[1]; [1]Hokkaido University

Theoretical calculation for phase equilibria is attempted for metal-hydrogen alloy system. A particular focus is placed on the formation of superabundant vacancies which has been reported in various metal-hydrogen alloys. The amount of vacancies introduced in the system is nearly 10-20%. The key to understand this anomaly is the binding energy between hydrogen and vacancy. A simple statistical thermodynamics theory which takes this energy into account is successful to grasp the essence of the phenomenon. In the present study, we further consider the wide range of configurational correlation effects by employing Cluster Variation Method. A preliminary study is attempted based on the two dimensional square lattice with Lennard Jones type atomic interactions. The free energy is optimized with respect to volume in addition to cluster probabilities. The results indicate the clear dependences of vacancy concentration on the content of hydrogen.

4:45 PM Invited
When Putting More Physics into CALPHAD Results also into Flavoring Physics with CALPHAD: *Suzana G. Fries*[1]; [1]SGF Scientific Consultancy

It is about 10 years ago that a call was done by W. A. Oates on the benefits of a more close cooperation between the different formalisms used by researchers interested in thermodynamic properties of solution materials. This closed interaction is being practised and although, in that time, the major gain was envisaged for the more pragmatic calphaders, nowadays it becomes clear that this pragmatism is not so crude and that theoretical methods can find inside the Calphad results some "realitycourse" where their predictions should lay. The progress done in these last years into the two directional linking (Calphad <->Physics) will be reported.

Lead Free Solder Implementation: Reliability, Alloy Development, and New Technology: Mechanical Behavior II: Creep

Sponsored by: The Minerals, Metals and Materials Society, TMS Electronic, Magnetic, and Photonic Materials Division, TMS: Electronic Packaging and Interconnection Materials Committee
Program Organizers: Nikhilesh Chawla, Arizona State University; Srinivas Chada, Medtronic; Sung K. Kang, IBM Corporation; Kwang-Lung Lin, National Cheng Kung University; James Lucas, Michigan State University; Laura J. Turbini, University of Toronto

Monday PM — Room: 214A
March 13, 2006 — Location: Henry B. Gonzalez Convention Ctr.

Session Chairs: James Perry Lucas, Michigan State University; Kejun Zeng, Texas Instruments

2:00 PM Invited
Creep and Mechanical Properties of Sn-Based Alloys for Microelectronics Solder Applications Using Impression and Other Test Techniques: G. S. Murthy[1]; S. Devaki Rani[2]; V. V. Subrahmanyam[1]; *K. Linga Murty*[3]; [1]Andhra University; [2]Jawaharlal Nehru Technological University; [3]North Carolina State University

A number of Sn-based alloys are selected as possible candidate materials to replace Pb-based alloys for microelectronics interconnects and solder applications. Many binary alloys along with a ternary Sn-57Bi-1.3Zn were examined along with Pb-Sn eutectic (for comparison) with emphasis on impression creep characteristics. In addition, the mechanical properties were determined along with wettability by evaluating the contact angles and substrate contact areas. In addition to the standard creep characteristics such as stress exponent (n) and activation enthalpy (H), the dependence of impression velocity (strain-rate) on impression size (diameter) were determined to assist in the interpretation of the underlying deformation mechanism(s). From these studies, it can be concluded that Sn-3.5Ag, Sn-9Zn and Sn-58Bi alloys are suitable substitutes for high temperature applications (such as for automotive technologies) while Sn-57Bi-1.3Zn alloy can be an effective non-toxic substitute for Pb-Sn eutectic generally considered for normal operatingconditions. A summary of ball indentation, lap shear as well as solder bump array (33x33) shear tests will be presented.

2:25 PM Invited
Creep Behavior of Lead Free Solder Interconnects: Creep Testing and Constitutive Modeling: *Indranath Dutta*[1]; Chanman Park[1]; Deng Pan[1]; Susheel Jadhav[2]; Ravi Mahajan[2]; [1]U.S. Naval Postgraduate School; [2]Intel Corporation

The creep behavior of ball grid array (BGA) or flip-chip (FC) solder joints during thermo-mechanical cycling often limits the reliability of microelectronic packages. In this paper, we present experimental creep results on pure Sn and two different compositions of SnAgCu solders, based on impression creep tests on BGA balls, with emphasis on microstructural effects on creep. Based on the above observations, a microstsrucTurally-adaptive creep model for solder interconnects undergoing in situ strain-enhanced coarsening will be presented. This model accounts for the effects of microstructural aging on the creep response of solder joints, and is capable of adjusting itself as solder joint microstructures evolve during service. Data on experimental determination of the relevant coarsening kinetics parameters for a SnAgCu solder will also be presented. Supported by NSF, SRC, and INTEL Corp.

2:50 PM
Microstructure and Mechanical Behavior of Novel Rare Earth-Containing Pb-Free Solders: *Martha A. Dudek*[1]; Rajen S. Sidhu[1]; Nikhilesh Chawla[1]; M. Renavikar[2]; [1]Arizona State University; [2]Intel Corporation

Currently several Pb-free material systems are available as replacements for traditional Pb-based solders in microelectronic packaging, including near eutectic combinations of Sn-rich alloys. Although these materials have been shown to have superior mechanical properties when compared to the Pb-Sn system, much work remains in developing these materials for electronic packaging. Small additions of rare-earth elements have been shown to improve the mechanical properties of Sn-rich solder. In this work we have investigated the effect of the addition of lanthanum (0.5 wt%) on the shear strength and creep behavior of a Sn-3.9Ag-0.7Cu alloy. Microstructure characterization of as-processed and reflowed samples was conducted in order to determine the influence of LaSn3 intermetallics on the mechanical properties. The effect of LaSn3 intermetallics in refining the microstructure of the Sn-Ag-Cu alloy and their role in creep resistance will be discussed.

3:10 PM
Nanoindentation on SnAgCu and SnCu Lead-Free Solder and Analysis: *Luhua Xu*[1]; John H. L. Pang[1]; [1]Nanyang Technological University

Nano-indentation charcterization on SnAgCu and SnCu solder was reported. The solder creep effect on the measured result was analyzed. Nanoindentation test with different maximum loads from 6 to 20mN, time-to-maximum-load from 1 to 100 seconds, hold time from 5 to 400 seconds, were studied. The penetration depth increases vs load and hold time due to creep effect was expressed with an empirical relationship. The pop-in phenomena was observed from load-displacement curve in the first 50-200nm penetration, which is related Sn lattice and boundary sliding. The unloading curve after different holding time were compared at the upper part, the unloading curves begin at higher depths for longer hold periods. It can be clearly seen that the unloading curve shows a bowing towards higher depth if the hold period is too short. An improved method was proposed for measuring Solder's Young's modulus, where the influence of creep can be neglected.

3:30 PM
Effects of Interfacial Intermetallics on Mechanical and Creep Properties on Thin Pb-Free Alloy Solder Joints: *James P. Lucas*[1]; [1]Michigan State University

Minimizing electronic packages also demands a concomitant thickness reduction of the solder joint itself that provides both mechanical and electrical connections of components to the substrate. For thin solder joints, the amount of interfacial intermetallic compound (IMC) increases in comparison to the actual solder volume in the joint. With aging isothermal and/or thermo-mechanical aging, the IMC layer may grow to comprise 80-90 percent of the solder joint volume. Nanoindentation testing (NIT) was used to investigate the mechanical properties of interfacial IMCs in ~ 50 mm-thick solder joints of several Sn-based eutectic and near-eutectic Pb-free solder alloys. Creep studies were performed on as-reflow and aged solder joints to determine the influence of the IMC layer thickness and compositional changes on resultant creep behavior. This investigation reports on the propensity of the IMC layer to affect subsequent mechanical properties in thin Pb-free solder joints.

3:50 PM Break

4:00 PM

Stress Relaxation of Sn3.5Ag Eutectic Alloy: *Fuqian Yang*[1]; Lingling Peng[1]; Kenji Okazaki[1]; [1]University of Kentucky

The localized stress relaxation of a Sn3.5Ag eutectic alloy was studied by using the impression technique in the temperature range of 393-488 K. The impression was made at prescribed indentation load and stopped at a certain depth of the indentation. The stress relaxation at different temperatures was recorded as a function of time. Using the dislocation dynamics, a relation between the punching stress and the relaxation stress rate was established. It was found that the dislocation velocity-stress exponent for the motion of dislocations is in a narrow range of 6.5 – 5.1 but decreases linearly with increasing temperature. The activation energy for the localized stress relaxation of Sn3.5Ag alloy is in the range from 38.1 to 48.4 kJ/mol. This research was supported by NSF through a grant DMR-0211706 monitored by Drs. Guebre Tessema and Bruce A. MacDonald.

4:20 PM

Effects of Specimen Volume of Solder on Creep Deformation: *Sung Bum Kim*[1]; Jin Yu[1]; [1]Korea Advanced Institute of Science and Technology

Creep characteristics of solders are very important to estimate real life time when the solders are subjected to thermal fatigue environment. However, great inconsistencies exist among creep data in literature due to the differences on specimen volume. As solder volume is smaller, the microstructural change of solders will happen because of higher solidification rate and effects of pad will be greater. In the present work, creep properties of Sn-3.5Ag solder alloy were investigated at 373K. To produce lap shear creep test samples, two FR4 PCBs with Cu pad were reflowed using Sn-3.5Ag alloy balls with various diameters. Moreover, double shear creep test specimen with uniformly shaped solder joints (uniform shear specimen) were also produced using three Cu plates. Experiments show that the minimum strain rate of lap shear specimen using 760μm is lower than that of uniform shear specimen by a factor of 10 due to different failure mechanism.

4:40 PM

Corrosion Resistance of Sn-Ag-Cu Solder Alloys: *Bo Li*[1]; Bin Zong[1]; Yaowu Shi[1]; Yongping Lei[1]; Zhidong Xia[1]; Fu Guo[1]; [1]Beijing University of Technology

The anti-corrosion behavior of Sn-Ag-Cu solder alloys was investigated in the present research. Corrosion resistance tests were conducted in a 5% NaCl solution. The corrosion resistance of Sn-Ag-Cu solder was quantified and compared with Sn-Zn and Sn-Pb solders according to the polarization curve and mass loss of the solder alloys. Morphological features of these alloys were characterized. The mechanism of causing such morphology change due to corrosion was analyzed from the phases formed in the microstructure of Sn-Ag-Cu, Sn-Zn, and Sn-Pb solders, respectively. The effect of rare-earth element addition on the corrosion resistance of Sn-Ag-Cu solder alloy was also investigated.

5:00 PM

Physics Based Reliability Model to Predict Solder Thermal Interface Material Performance in Microelectronic Packages: *Arun Raman*[1]; Shubhada Sahasrabudhe[1]; Vikram Bala[1]; Sankara Subramanian[1]; Ashish Gupta[1]; Carl Deppisch[1]; Sridhar Narasimhan[1]; [1]Intel Corporation

Metal-based solder thermal interface material (TIM) is utilized in microelectronic packages for efficient thermal performance. Temperature cycling can affect solder TIM performance. This work focuses on development of a predictive phenomenological reliability model for solder TIM degradation. Metallization of integrated heat spreader (IHS) and backside of Si die facilitates adhesion of solder TIM to both surfaces through the formation of metallurgical bonds. Temperature cycling causes interfacial degradation between intermetallic compounds that are created and bulk solder, leading to thermal performance deterioration. In this study, finite element models based on cohesive elements at the interfaces were developed to predict damage growth through temperature cycling and subsequently to predict thermal performance using thermal finite element models. Validation was performed on experimental builds, using techniques such as acoustic microscopy and electron microscopy. Based on the degradation physics, this reliability model enables solder TIM life prediction eliminating the need for extensive empirical builds.

5:20 PM

Examination of the Microstructure and Failure Mechanisms of Pb Free Solder Joints: *Eric J. Cotts*[1]; L. P. Lehman[1]; Peter Borgesen[2]; [1]Binghamton University; [2]Universal Instruments Corporation

The microstructure, mechanical properties and reliabilities of ball grid array (BGA), chip scale packaging (CSP), and flip chip components with SnAgCu solder joints were examined as a function of undercooling, and subsequent thermal cycling. Assemblies were removed for cross sectioning and microstructural characterization after different degrees of undercooling (during the initial reflow profile), and later, at various stages of cycling. The microstructures of these different samples were examined by means of optical and scanning electron microscopy. The Sn dendrite arm width was observed to monotonically increase with solder ball diameter. Polarized light microscopy provided delineation of Sn grains, while electron microscopy with EDS provided compositional analysis. The variation in the thermomechanical loads with solder joint location across an area array allowed detailed study of a range of temperature-damage combinations.

5:40 PM

Flip Chip Bonding on Glass and Plastic Substrates Using Sn Bumps and NCAs: *Zhigang Chen*[1]; Bae Yong Kim[1]; Sang Mok Lee[1]; Young-Ho Kim[1]; [1]Hanyang University

This study presented the reliability results of NCA applied COG and COP processes. PES was selected as the plastic substrate. Sn bumps were employed especially for its excellent deformation ability, which was capable of compensating for ununiformity of the bumps height, and being featured as low cost flip chip bonding technique. Thermal cycling tests were carried out between temperatures of 0°C and 100°C. The COG specimens sustained by 1000 cycles without failure and the variation of resistance followed an increasing trend. Comparatively, the average contact resistance of COP specimens descended in the early stage of the cycling test and then leveled off. This beneficial change is owing to the postcuring of NCA during thermal cycling and flexibility of PES, as well as further and sufficient interdiffusion between bumps and pad. This work was supported by Korea Research Foundation Grant(KRF-2004-005-000164).

Magnesium Technology 2006: Automotive and Other Applications

Sponsored by: International Magnesium Association, TMS Light Metals Division, TMS: Magnesium Committee
Program Organizers: Alan A. Luo, General Motors Corporation; Neale R. Neelameggham, US Magnesium LLC; Randy S. Beals, DaimlerChrysler Corporation

Monday PM Room: 6B
March 13, 2006 Location: Henry B. Gonzalez Convention Ctr.

Session Chairs: Randy S. Beals, DaimlerChrysler Corporation; Gerald S. Cole, LightWeightStrategies LLC

2:00 PM
Building a Mg Intensive Engine: A Progress Report on the USAMP Mg Powertrain Cast Components Project: *Joy A. Hines*[1]; John E. Allison[1]; Robert C. McCune[1]; Randy S. Beals[2]; Lawrence Kopka[2]; Bob R. Powell[3]; Larry Ouimet[3]; William L. Miller[3]; Peter P. Ried[4]; [1]Ford Motor Company; [2]DaimlerChrysler; [3]General Motors Corporation; [4]Ried and Associates, LLC

Over the past five years, USAMP has brought together representatives from Daimler-Chrysler, General Motors, Ford Motor Company and over 40 other participant companies from the Mg casting industry to create and test a low cost Mg alloy engine that would achieve a 15–20% weight savings without compromising performance as compared with an equivalent Al engine. In this program, a 2.5L Ford Duratec engine assembly was modified to create a Mg version. The block, oil pan, front cover, and bed plate were redesigned to take advantage of the properties of both HPDC and sand cast Mg creep resistant alloys. This talk will discuss the alloy selection process and the casting and testing of these new Mg-variant components. This talk will also examine the lessons learned and implications of this pre-competitive technology for future applications.

2:20 PM
AM-HP2: A New Magnesium High Pressure Diecasting Alloy for Automotive Powertrain Applications: *Colleen Bettles*[1]; Mark Gibson[1]; Gordon Dunlop[2]; Morris Murray[2]; [1]CAST Cooperative Research Centre; [2]Advanced Magnesium Technologies

AM-HP2 is a new magnesium diecasting alloy that has been specially developed to provide good diecastability and creep resistance at temperatures in the range 150-200ºC. This temperature range is important for many automotive powertrain applications. AM-HP2 was developed to have similar properties to the very successful sandcasting alloy AM-SC1 but with modifications to ensure excellent diecastability. The alloy was developed in recognition of high pressure die casting's advantages of higher production rates and lower manufacturing costs compared to sand casting. AM-SC1 is most suitable for production of prototypes and small production runs (as for the V6 engine block of the USCAR MPCC program) while AM-HP2 provides similar properties in the diecast condition. This paper compares the properties of AM-HP2 with other commercially available high temperature creep resistant magnesium alloys.

2:40 PM
Wrought Magnesium Alloys for Structural Applications: *Alan A. Luo*[1]; Anil K. Sachdev[1]; [1]General Motors Corporation

While high-pressure die casting is the dominant process for current magnesium applications, wrought magnesium alloys are receiving increasing attention from academia and industries. As magnesium is expanding to more critical structural applications in automotive body and chassis systems, there is a great need for developing wrought magnesium products to provide improved mechanical and physical properties and corrosion resistance. This paper summarizes recent wrought magnesium alloy development, grain refinement in billet production, extrusion process optimization, and moderate temperature bending and forming of magnesium tubes. An extensive investigation was carried out to determine the effect of microstructure on the deformation mechanisms of wrought magnesium alloys at a moderate temperature range (100-200°C). The roles of strain-hardening, twinning and slip in deformation and formability of magnesium alloys will be discussed.

3:00 PM
Fabrication of Carbon Long Fibre Reinforced Magnesium Parts in High Pressure Die Casting: *Gerald Klaus*[1]; Christian Oberschelp[1]; Martin Fehlbier[1]; Andreas Bührig-Polaczek[1]; Jens Werner[2]; Werner Hufenbach[2]; [1]Aachen University; [2]Dresden University

There is an increasing demand for light weight structural parts, which are able to fullfill increased high temperature properties combined with advanced wear resistance. These requirements can be achieved by carbon long fibre reeinforced magnesium parts. Within the development of an industrial scale process for fibre infiltration and integration of preinfiltrated metal matrix composites, a suitable high pressure die casting method is under evaluation at the facilities of the Foundry Institute of RWTH Aachen University. The special challenge of high melt velocity and pressure is taken into account and requires innovative solutions, brought forward in this project. A new electric fibre heating system has been implemented in the process to assist infiltration, as well as a new special two step clamping device, which ensures proper fit. As a great advantage of this new method, the fibre preforms are preheated in the closed die under protective atmosphere/vaccum, till casting takes places.

3:40 PM
Machining of Hybrid Reinforced Mg-MMCs Using Abrasive Water Jetting: Eckhard Aust[1]; Maxim Elsaesser[1]; *Norbert Hort*[1]; Wolfgang Limberg[1]; [1]GKSS Research Centre

Magnesium based Metal Matrix Composites (MMCs) reinforced by a combination of short Al2O3-fibres and SiC-particles are promising constructional materials due to the low density and thermal expansion, high creep and wear resistance. Such a material is the hybrid reinforced magnesium alloy AE42, which is produced by the melt infiltration of fibre-particle preforms in the squeeze casting process. Many problems arise by machining these preforms with common machining tools because of the high wear resistance caused by the ceramic reinforcement. Solutions are only expensive tools with cutting edges made of polycrystalline diamonds or CVD-diamond coatings. This work is focussed on the application of abrasive water jet cutting for machining these wear resistant MMCs. Cutting tests were performed at MMC-specimens with thickness of 2 – 25 mm. Experimental results are presented which clearly indicate the high potential and efficiency of the abrasive water jet for machining MMCs.

3:20 PM Break

4:00 PM
The Influence of Mechanical Activation on the Process of Thermal Reduction of SiO2 by Mg Powder: *Nshan Hovhannes Zulumyan*[1]; Agasy Torosyan[1]; Anna Rafael Isahakyan[1]; Zaruhi Hayk Hovhannisyan[1]; [1]IGIC NAS RA

Solid state chemical reaction in SiO2 – Al stoichiometric mixture induced by heat treatment at the temperature 350-400°C has been investigated, depending on the time of mixture's preliminary mechanical processing and activation. It's necessary to note that SiO2 is an aqua silica gel extracted from serpentinites using a new thermo-chemical method of the serpentinous ultra basic rocks treatment. Different thermal analysis (DTA) and X-ray diffraction (XRD) have shown that the displacement reaction is occurring with forming mainly nanocrystalline magnesium oxide (MgO) and silicon (Si) and partly forsterite (Mg2SiO4). Magnesium oxide and forsterite can be easily removed by means of decantation. The quantities of forming products depend on the parameters of mechanical processing. Optimal parameters have been found in order to provide occurring reaction.

4:20 PM Cancelled
Hydrogen Production by Using Ni-Rich AZ91D Recycled Ingot

4:40 PM
Synthesis of Magnesium Diboride Powder by Self-Propagating High-Temperature: *Huimin Lu*[1]; Huanqing Han[1]; Ruixin Ma[1]; Yongheng Wang[1]; [1]University of Science and Technology Beijing

Self-propagating high-temperature synthesis (SHS) method was used to fabricate MgB2 powder from Mg-B system. In this paper, the reaction process of Mg and B was studied by thermodynamic calculation, X-ray

diffract-meter and micro-image analyzer. These results show that the single-phase MgB2 can be synthesized by self-propagating high-temperature synthesis method. When Mg and B react, Mg firstly melts and then reacts with B to form MgB2; but if the synthesis temperature is too high, MgB2 can decompose into MgB4 and Mg. These synthesized MgB2 particles appear random geometry and fine crystal grain. At normal pressure, the decomposition temperature of MgB2 is less than 1320K; but higher gas pressure is beneficial to lifting the decomposition temperature of MgB2. And at high temperature, there are these phenomena that MgB2 can also exist or MgB2 directly decomposes into Mg and amorphous B.

5:00 PM

Surface Cladding of Magnesium Alloy Castings Using Nd:YAG Laser: *Xinjin Cao*[1]; Min Xiao[1]; Mohammad Jahazi[1]; [1]Institute for Aerospace Research

Magnesium alloys have low hardness, wear and corrosion resistance. With their increased applications in aerospace, aircraft, automotive, electronics and other industries, the surface cladding and repair of magnesium alloy components will become significant. The high heat-input energy associated with conventional arc processes, however, results in large variations in metallurgical structures, large heat affected zone and fusion zone, high shrinkage, high evaporative rates and loss of alloying elements, high residual stresses and distortions. Compared with the arc techniques, high energy-density laser beam has the potential to avoid such shortcomings and thus become an important technique to clad and repair magnesium components. The objective of the present study is to investigate the possibility of laser cladding and repair for ZE41A-T5 sand castings using EZ33A welding wires. This presentation will report on the progress in laser cladding obtained in the Aerospace Manufacturing Technology Center of the NRC Institute for Aerospace Research.

Magnesium Technology 2006: Casting and Solidification I

Sponsored by: International Magnesium Association, TMS Light Metals Division, TMS: Magnesium Committee
Program Organizers: Alan A. Luo, General Motors Corporation; Neale R. Neelameggham, US Magnesium LLC; Randy S. Beals, DaimlerChrysler Corporation

Monday PM
March 13, 2006

Room: 6A
Location: Henry B. Gonzalez Convention Ctr.

Session Chairs: John Hryn, Argonne National Laboratory; Helmut Kaufmann, LKR ARC Leichtmetallkompetenzzentrum

2:00 PM

A Directional Solidification Study of Mg-4Al and AXJ530 Alloys: *Chuan Zhang*[1]; Dong Ma[1]; Kaisheng Wu[2]; Hongbo Cao[1]; Guoping Cao[1]; Sindo Kou[1]; Y. Austin Chang[1]; [1]University of Wisconsin; [2]CompuTherm, LLC

A binary magnesium alloy with 4 wt% Al (Mg-4Al) and a commercial alloy AXJ530 with a base composition of Mg-5Al-3Ca have been investigated using the directional solidification technique. The ability to producing uniform microstructures in directional solidification enables us to correlate the formation of the microstructure and its characteristic length scales (e.g. primary dendrite arm spacing) quantitatively with processing parameters, such as the growth rate (or the solidification front speed that scales with the applied cooling rate). Notably a wide range of cooling rates from 0.02 to 4 K/s are attainable by our DS apparatus, which correspond to the growth rates from 5 to 1000 mm/s at a fixed temperature gradient of 4.0 K/mm. In this presentation, we will report the experimental results obtained as well as the theoretical analysis.

2:20 PM

Experimental Study of Vacuum Die Casting Process of AZ91D Magnesium Alloy: Bo Hu[1]; *Shou-Mei Xiong*[1]; Masayuki Murakami[2]; Yoshihide Matsumoto[2]; Shingo Ikeda[2]; [1]Tsinghua University; [2]TOYO Machinery and Metal Company Ltd.

The effect of operation conditions in vacuum die casting process on the porosity and mechanical properties of die cast parts of AZ91 alloy were investigated. Standard tensile test specimens and step-shape test plates were cast on a TOYO BD-650-V4-N cold chamber die casting machine. Five vacuum levels from 5kPa to 80kPa, as well as the non-vacuum condition, were used and five levels of casting pressure from 22.7MPa to 66.7MPa were applied during the experiments. Other operation conditions were kept constant. Pressure measurements at different positions inside the cavity were made during the work cycle. Density, tensile strength and heat treatment results were analyzed. Relationship between mechanical properties of the cast parts and process parameters were discussed and the result show that vacuum application to the die casting process of AZ91D magnesium alloy could not only improve the mechanical properties of castings but also reduce the tonnage requirement of the equipment.

2:40 PM

Hot Cracking Susceptibility of Binary Mg-Al Alloys: Guoping Cao[1]; *Sindo Kou*[1]; Y. Austin Chang[1]; [1]University of Wisconsin

The susceptibility of binary Mg-Al alloys in permanent mold casting was tested, including Mg-0.25Al, Mg-0.6Al, Mg-1Al, Mg2Al, Mg-4Al and Mg-8Al (all in wt %). A steel mold was used for constrained rod casting, in which rods of various lengths were cast with sudden enlargement at both ends of each rod to prevent it from free contraction during solidification and thus induce hot cracking. The hot cracking susceptibility was evaluated based on the widths and locations of the cracks observed. The curve of crack susceptibility vs. Al content was determined and compared with previous curves based on ring casting in steel molds and constrained rod casting in sand molds. The Scheil model of solidification was used to calculate the curves of temperature vs. fraction solid of the alloys. Possible correlations between the crack susceptibility curve and the curves of temperature vs. fraction solid will be explored.

3:00 PM

Phase Equilibria of Mg-Al-Ca Ternary System at 773 and 673 K: *Akane Suzuki*[1]; Nicholas D. Saddock[1]; J. Wayne Jones[1]; Tresa M. Pollock[1]; [1]University of Michigan

Isothermal sections of the Mg-Al-Ca ternary system at 773 and 673 K were determined with consideration of the existence of the ternary $(Mg, Al)_2Ca$ compound with C36 structure. Alloys with compositions Mg-(0~18.8)Al-(1.8~13.4)Ca and Mg-(0~66.7)Al-33.3Ca (at%) were equilibrated and analyzed by EPMA and TEM. The C36 phase exists between C14 (Mg_2Ca) and C15 (Al_2Ca) phases, and its stoichiometry is close to $Mg_2Al_4Ca_3$. The α-Mg phase equilibrates with C14 and C36 phases at 773 K, but with C14, C15 and β phases at 673 K. This is due to the decomposition of the C36 phase into C14 and C15 phases between these temperatures. Each intermetallic phase has significant solid-solubility in the ternary system. The microstructural stability in the vicinity of the α-Mg grain boundaries will be also discussed in terms of relative change in the eutectic structures containing C14, C36 or β phases during annealing.

3:20 PM

Preliminary Investigation on the Formation and Grain Refinement of Particles in Mg-Al Alloys: G. Klösch[1]; B. J. McKay[1]; *Peter Schumacher*[2]; [1]Austrian Foundry Research Institute; [2]University of Leoben

Grain refinement with Zirconium addition is commonly used for non aluminum containing Magnesium alloys. However, Mg-Al alloys with Zirconium addition are assumed to be affected by a poisoning effect leading to the formation of Al3Zr. The present paper describes the effects on the grain size of Mg-Al alloys by refinement with refractory metals (Zr, Ti) and in-situ formed ZrB2 particles. Due to the excellent crystallographic orientation compared to Mg and the high thermal stability of ZrB2 grain refinement is observed when sufficient growth restriction by Ti and Zr is present. This paper gives preliminary results on the formation, nucleation and poisoning mechanism in Mg-Al alloys with Zr addition. Moreover, particles were added to the Mg-Al melt to compare the efficiency of the in-situ formed ZrB2 particles. Samples were taken according to the TP1 test procedure and grain size measured with the intersect method.

3:40 PM

Property Variation in Thin Walled Magnesium Die Cast Components: *Saravanan Subramanian*[1]; Patrick Blanchard[1]; Nicholas Warrior[2]; James DeVries[1]; [1]Ford Motor Company; [2]University of Nottingham

Utilization of magnesium within vehicle design offers substantial opportunity to reduce mass. This has resulted in a wide range of automotive applications. More recently the scope of application has been extended to include components that are considered crash critical. This introduces the problem of how to design effectively using a process that is reported to produce parts that exhibit large local variations in part properties. In order to understand the key factors that contribute to this, a micro-structural examination was performed on a high pressure die cast component to investigate the root cause of property variation. Properties of interest include yield strength, failure strain and bulk density. This paper discusses the influences of microstructure and porosity on mechanical property variation, and identifies key factors that influence final performance. Further discussion also includes proposed methods of reducing property variation using advances in process control.

4:00 PM Break

4:20 PM

Solidification Characteristics and Creep of Permanent Mold Cast Mg-Al-X Ternary Alloys: *Nicholas D. Saddock*[1]; Akane Suzuki[1]; Jessica R. TerBush[1]; Eric C. Heininger[1]; J. Wayne Jones[1]; Tresa M. Pollock[1]; [1]University of Michigan

A permanent mold casting technique has been developed to cast tensile creep specimens of Mg – Al – X: (Ca, Sr, Ce, La) ternary alloys. Solidification behavior and microstructure have been analyzed in each of these alloys. Electron microprobe analysis (EPMA) was conducted on as-cast Mg – 4 Al – 4 X alloys (wt.%) to investigate the partitioning of each alloying element to the α grain interior and grain boundary regions. Segregation behavior during solidification and, in particular, the influence of ternary additions on aluminum partitioning was described using a modified Scheil model. Creep behavior of the permanent mold cast alloys was studied and the role of grain boundary microstructure on creep behavior in these alloys will be described.

4:40 PM

Phenomena of Formation of Gas Induced Shrinkage Porosity in Pressure Die-Cast Mg-Alloys: *Soon Gi Lee*[1]; Arun M. Gokhale[1]; [1]Georgia Institute of Technology

It has been known that the formation of gas and shrinkage porosity has different dependencies on the process conditions, and consequently, the gas and shrinkage pores are usually regarded as independent microstructural attributes. In this contribution, it is shown that in high-pressure die-castings gas pores can lead to the formation of shrinkage porosity under specific conditions. This is because the air/gas in the gas porosity is an efficient heat-insulating medium. Therefore, the presence of gas porosity can retard the heat transfer in the liquid melt as compared to similar regions without gas porosity. Consequently, the local solidification rate is lower in such region, leading to shrinkage porosity formation. The two and three-dimensional (3D) microstructural observations using digital image analysis and numerical simulation for heat transfer support such a hypothesis. Further, the finite element (FE)-based simulations have been performed on the 3D microstructures to reveal the variations of local stress caused by gas induced shrinkage porosity.

5:00 PM

Overview of the Magnesium Casting Industry Technology Roadmap: The Road to 2020: *John N. Hryn*[1]; Steve Robison[2]; David J. Weiss[3]; Bruce Cox[4]; Katie Jereza[5]; Ross Brindle[5]; [1]Argonne National Laboratory; [2]American Foundry Society; [3]ECK Industries Inc; [4]Daimler Chrysler Corporation; [5]Energetics Incorporated

The American Foundry Society Magnesium Division has led an effort to develop the Magnesium Casting Industry Technology Roadmap. Completed in September 2005, the Roadmap outlines the industry's strategic technology agenda for the next 15 years, focusing on three principal components: (1) improved process technologies that lead to greater productivity and efficiency while delivering consistent, high-quality castings at competitive costs; (2) enhanced information management and sharing to accelerate technological innovation and transfer, and, (3) increased infrastructure development. Experts from across the magnesium casting industry identified R&D needs in each of these areas, indicated the highest priorities, and stratified these needs by time frame. In total, the Roadmap identifies more than 60 R&D needs and offers detailed action plans for the six highest-priority activities. This paper highlights key concepts presented in the Roadmap.

Materials in Clean Power Systems: Applications, Corrosion, and Protection: Hydrogen Separation, Delivery, and Materials Issues in Clean Power Plants

Sponsored by: The Minerals, Metals and Materials Society, TMS Structural Materials Division, TMS/ASM: Corrosion and Environmental Effects Committee

Program Organizers: Zhenguo Gary Yang, Pacific Northwest National Laboratory; K. Scott Weil, Pacific Northwest National Laboratory; Michael P. Brady, Oak Ridge National Laboratory

Monday PM — Room: 212B
March 13, 2006 — Location: Henry B. Gonzalez Convention Ctr.

Session Chairs: Iver E. Anderson, Iowa State University; Ken Natesan, Argonne National Laboratory

2:00 PM Invited

Inorganic Membranes for Energy-Related Gas and Water Purification: *Henk Verweij*[1]; [1]Ohio State University

Inorganic membranes consist of a stand-alone or supported material with special transport properties, able to operate at elevated temperatures and pressures. Relevant separations that can be conducted with inorganic membranes are H_2, H_2O and O_2 from other gases, and water purification. Separation of CO_2 from other gases is currently considered. Inorganic membranes are classified according to the presence and size of connected porosity. Dense membranes have 100% selectivity for H_2 and O_2, and acceptable flux at high temperature. Micro-porous membranes have <2 nm pores and combine high selectivity with fairly high fluxes at lower temperatures. Meso-porous membranes have 2-50 nm pores and have a good thermo-chemical stability, moderate selectivity and very high fluxes over a wide temperature range. To make inorganic membranes a viable option the research focus must be directed towards thermochemical stability and operation at relevant conditions, and development of <100 nm defect-free supported membrane structures.

2:30 PM Invited

Materials for Hydrogen Delivery: Embrittlement Problems and Remediation: *Petros Sofronis*[1]; I. M. Robertson[1]; [1]University of Illinois, Urbana-Champaign

The technology of large scale hydrogen transmission from central production facilities to refueling stations and stationary power sites is at present undeveloped. Among the problems which confront the implementation of this technology is the deleterious effect of hydrogen on structural material properties, in particular at gas pressure of 1000 psi which is the desirable transmission pressure suggested by economic studies for efficient transport. To understand the mechanisms of hydrogen embrittlement our approach integrates mechanical property testing, TEM observations, and finite element modeling. A discussion is presented on how we can develop and verify a lifetime prediction methodology for failure of materials used for pipelines and welds exposed to high-pressure hydrogen. Development of such predictive capability and strategies is of paramount importance to the rapid assessment of using the natural-gas pipeline distribution system for hydrogen transport and of the susceptibility of new alloys tailored for use in the new hydrogen economy.

3:00 PM

Surface Engineering of Sliding Contacts in the Hydrogen Service Environment: *James D. Holbery*[1]; Peter Blau[2]; Laura Riester[2]; [1]Pacific Northwest National Laboratory; [2]Oak Ridge National Laboratory

Sliding metal surface contacts within a 100% Hydrogen environment poses a service challenge due to the hydride formation at the surface causing surface impingement resulting in an increased material-pair friction coefficient. In addition, material integrity at the surface interface will be altered as a function of Hydrogen exposure. In order to begin to understand material behavior in the Hydrogen service environment, we have

constructed a pressure vessel capable of 100% exposure at pressures up to 31 MPa and temperatures as high as 100ºC for durations exceeding several hundred hours. In addition, we have developed the ability to measure sliding contact friction utilizing Friction Force Microscopy within a 100% Hydrogen environment, the first such instrument configuration known to the authors at this time. As a result, we have analyzed a series of material surfaces to determine the degradation of surface properties due to Hydrogen exposure. By comparing these results with localized surface modulus properties developed utilizing nanoindentation and other analytical results, we will present data that has enabled us to begin to understand the impact of hydride formation on material sliding contacts that will serve a critical role in transporting, distributing, combusting, and managing Hydrogen.

3:25 PM
Hydrogen-Rich Gas Production from Gasoline in a Short Contact Time Catalytic Reactor: *Ludmilla Bobrova*[1]; Ilya Zolotarsky[1]; Vladislav Sadykov[1]; Vladimir Sobyanin[1]; [1]Boreskov Institute of Catalysis

The research concerns the problems emerged from a short contact time adiabatic reactor operation in a pilot plant scale. Hydrogen-rich gas was generated by selective catalytic oxidation of isooctane and gasoline over original monolithic catalysts with the different supports. Thermodynamic analysis was employed with a purpose of determining the operational parameters, maximum hydrogen yield, and adiabatic temperature rise available. Gasoline, which contains 191 types of hydrocarbons, was simulated by a mixture of 28 organic compounds. It was demonstrated, that over the range of operational parameters required for syngas generation, equilibrium synthesis gas was produced over the catalysts employed. However, some drawbacks can make the main catalytic process being complicated. Pre-reforming of fuel with releasing of some chemical energy before the catalytic monolith can occur in reactor. Breakthrough of the feed arises near the reactor wall in a certain case. Feed composition, superficial velocity and reactor design features affect the phenomena mentioned.

3:50 PM Break

4:05 PM Invited
High-Temperature Materials Issues in Syngas/Hydrogen-Fired Turbines: *Ian G. Wright*[1]; Thomas B. Gibbons[2]; Adrian S. Sabau[1]; Bruce A. Pint[1]; [1]UT-Battelle; [2]Consultant

The combination of gasification technology with a gas turbine combined-cycle system can produce electricity from coal in a significantly more environmentally-friendly way, and at higher efficiencies than are possible with the technologies currently deployed. Because coal contains more carbon, and a higher level (and much wider range) of impurities than natural gas, there are challenges to be met to provide a sufficiently clean combustion process to allow the reliable operation of the gas turbine at the high temperatures needed for maximum efficiency. This paper addresses some specific issues associated with the durability of the hot gas path components in the gas turbine resulting from (1) differences in the thermal environment when combusting natural gas, syngas, or hydrogen-enriched syngas; (2) the potential for deposition, erosion, and/or corrosion when firing syngas; and (3) the tendency for increased interdiffusion of any protective metallic coating with the alloy substrate when operating at high temperatures.

4:35 PM Invited
Advanced Alloys for Compact, High-Efficiency, High-Temperature Heat-Exchangers: *Philip J. Maziasz*[1]; [1]Oak Ridge National Laboratory

ORNL has for several years focused on the behavior and performance improvements of sheets and foils of various alloys for compact heat-exchangers (recuperators) for advanced microturbines. Performance and reliability of such thin sections are challenged at 650-750°C by fine grain size causing excessive creep, and moisture effects greatly enhancing oxidation attack in exhaust gas environments. Alloys have been identified which can have very good properties for such heat-exchangers, with careful control of microstructure during processing, including alloy 625, HR120 and the new AL20-25+Nb. These alloys, or the mechanistic understanding behind their behavior, are also applicable to the heat-exchanger technology needed for fuel cell or other high-temperature, clean-energy applications. Research at ORNL is sponsored by the U.S. Department of Energy, Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Power Technologies, Microturbine Materials Program, under contract DE-AC05-00OR22725 with UT-Battelle, LLC.

5:05 PM
Effect of Atmosphere Composition on the High Temperature Oxidation of Chromia Forming Alloys: *Michael Haensel*[1]; Emmanuel Essuman[1]; Joanna Zurek[1]; Marek Michalik[1]; Lorenz Singheiser[1]; Willem J. Quadakkers[1]; [1]Forschungszentrum Juelich

The oxidation behaviour of pure chromium, Ni25Cr and the NiCr ODS alloy MA745 during isothermal exposure in Ar-O2- and Ar-H2-based gases containing various amounts of steam was studied at 1000 and 1050oC. The kinetics of scale growth during the isothermal exposure and the scale spalling during subsequent cooling were investigated by thermo gravimetry. The scale growth and morphology and adherence depend on the test gas composition. Scales formed on pure Cr and Ni25Cr in Ar-20%O2 were thinner, less adherent and showed more substantial porosity than those formed in steam containing gases. Differences in scale growth rates and morphology can be explained by formation of H2O/H2 bridges in scale voids. The growth mechanisms of Ni25Cr seems to be different from those for pure Cr. The oxidation rate of MA754 were found to be much smaller than that of Ni25Cr. The ODS alloy exhibited very thin oxide scales in all test environments.

Materials Processing Fundamentals: Solidification and Deformation Processing

Sponsored by: The Minerals, Metals and Materials Society, TMS Extraction and Processing Division, TMS: Process Fundamentals Committee, TMS: Process Modeling Analysis and Control Committee
Program Organizers: Princewill N. Anyalebechi, Grand Valley State University; Adam C. Powell, Massachusetts Institute of Technology

Monday PM — Room: 203A
March 13, 2006 — Location: Henry B. Gonzalez Convention Ctr.

Session Chair: Prince N. Anyalebechi, Grand Valley State University

2:00 PM
Comparative Study of the Effects of Solidification Rate on the Cast Microstructures of Aluminum Alloys 6016 and 6009: *Princewill N. Anyalebechi*[1]; [1]Grand Valley State University

The effects of solidification rate on the cast microstructures of aluminum alloys 6009 and 6016 have been investigated with directionally cooled laboratory-size ingots at ranges of solidification rate within those observed in commercial-size ingots. In both alloys, the average dendrite cell size and second phase particle size decreased with increase in average solidification rate and with a decrease in average local solidification time. However, at comparable solidification rates, the dendrite cells and second phase particles are finer in the shorter freezing range alloy 6009 than in the longer freezing range alloy 6016. This is provisionally attributed to the earlier formation of second phase intermetallics at higher temperatures during solidification and to the formation of greater amount of the relatively coarse plate-like beta-phase (Al9Fe2Si4) phases in alloy 6016. In general, the types and relative amounts of the second phase particles formed in both alloys are independent of solidification rate.

2:25 PM
The Effects of Internal Convection on the Lifetime of the Metastable Phase in Undercooled Fe-Cr-Ni Alloys: *Alaina B. Hanlon*[1]; D. M. Matson[2]; R. W. Hyers[1]; [1]University of Massachusetts; [2]Tufts University

When sufficiently undercooled, Fe-12wt%Cr-16wt%Ni alloys can undergo two-step solidification in which a metastable ferrite phase forms first, followed by the stable austenite phase. Two different levitation techniques show dramatically different lifetimes of the metastable phase. If the lifetime is too short, the sample will have an unfavorable mixed microstructure of fine grains where the sample underwent two-step solidification and dendrites where the melt solidified directly to the stable phase. Prior work has excluded many potential explanations for the difference observed in the metastable phase lifetime. The remaining hypothesis for this difference is dendritic interactions as a result of strong induced con-

vection. If the primary arms of the dendrites deflect enough, secondary arms of adjacent dendrites can collide, triggering early stable phase nucleation. Computational fluid dynamics along with experimental findings show that the difference in induced convection between the different processing methods is the reason for this difference.

2:50 PM

Age Hardening Behavior of AA2618: Hui Lu[1]; Puja B. Kadolkar[2]; Kozo Nakazawa[1]; *Teiichi Ando*[1]; Craig Alan Blue[2]; [1]Northeastern University; [2]Oak Ridge National Laboratory

The structural changes in solutionized AA2618 during natural aging and their effects on subsequent artificial aging were investigated by hardness measurements and X-ray diffraction. The changes in lattice parameter and hardness during natural aging indicate that copper-enriched clusters form primarily in the earliest stage, followed by the formation of magnesium-enriched clusters and copper-magnesium co-clusters. Prior natural aging consistently weakened the hardening during subsequent artificial aging at 180, 200 and 230°C but had no effects on artificial aging at 150°C. The decreased age hardening was attributed to the reversion of small clusters or zones that formed during prior natural aging. The lattice parameter exhibited erratic changes during the early stages of artificial aging, reflecting the reversion and the complex sequence of precipitation.

3:15 PM

Metallic Wires Elaboration Directly from Thin Liquid Jets: *Ludovic Charpentier*[1]; Yves Du Terrail-Couvat[1]; Yves Delannoy[1]; Christian Trassy[1]; [1]Electromagnetic Processing of Materials Laboratory

Elaborating metallic wires directly from liquid jets would avoid drawbacks of extrusion (space needed, damaging, cost…) and enable recycling. But liquid jets tend to break, due to capillary instabilities, unless a solid layer (coating or start of solidification) surrounds it. We recently developed a process to elaborate tin wires, cooled by water flow parallel to the jet. Superficial oxidization of tin produces a glass coating around the jet. Studies showed the length of wires increased when increasing speed of tin jets, and that water average speed should be the closest possible to the jet one to have smooth fibers. Producing 1 mm diameter wires is possible. The length of wires is limited by the experimental setup, which does not provide possibilities to coil the wire. Most of other metals do not generate glass-like oxides. The lack of coatings makes it necessary to reduce the capillary instabilities to obtain fibers.

3:40 PM Break

3:55 PM

Study of the Metallizing of the Continuous Carbon Fiber Surface: *Tianjiao Luo*[1]; Yao Guangchun[1]; Wu Linli[1]; [1]Northeastern University

Abstract: The electroless copper plating process for continuous carbon fiber using CuSO4•5H2O as the main salt and formaldehyde as reducing agent was experimentally studied, including the effects of pH values and concentration of chelating agents, additives and reducing agent on the electroless plating process. The surface morphology and composition of coating were investigated by means of Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDS), and deposited the coating thickness was measurated by way of dissolution. The results indicated that the pretreatment of carbon fiber before plating is so important that it is able to prevent from the " black core " phenomenon. With the process parameters got and optimized experimentally, the carbon fiber plated with copper shows homogeneous coating with favorable mechanical properties due to stable bath, such as the high bonding strength of coating.

4:20 PM

Research on a New Wearable and Electric Material Used in Current Electric Locomotive: *Lian Wei Yang*[1]; Guang Chun Yao[1]; [1]Northeastern University

Pantograph slide plate is quite important collecting electricity material of electric locomotive. A new one is developed in view of the existing problems of current pantograph slide plates. The new pantograph slide plate is consisted of copper, carbon fiber, graphite etc. And the influence of pressure and sintering temperature to the performance of pantograph slide plate is studied firstly. Then its performance of friction, abrasion and impact toughness is tested. Performance of the new pantograph slide plate is contrasted to current pantograph slide plates at last. The results showed the optimal technique of preparing slide plate. Its performance is improved greatly with friction coefficient reduced by 54.5%, abrasion ratio decreased by 41%, impact toughness increased by 9.6 times and conductance increased by 87 times compared with carbon slide plate C26.

4:45 PM

Characterization of Mechanical Properties and Microstructure in Copper Nanopowder Alloyed Al7075 T651 via Friction Stir Process: *Dongok Kim*[1]; Jianhui Wu[2]; William F. Schmidt[2]; Ajay P. Malshe[2]; [1]Korea Automotive Technology Institute; [2]University of Arkansas

Regardless of the advantages of Friction Stir Process (FSP), for age-hardened aluminum alloys, the mechanical properties such as hardness in the stir zone were decreased after FSP due to the growth or dissolution of strengthening precipitates. Here, as a new technique, FSP was introduced to alloy copper nanopowders in Al7075 T651. Mechanical properties together with micro and nanostructures were compared with as-FSPed Al7075 T651 using SEM, TEM, and Vickers hardness tests to understand structure-property relationships. It was shown that the Vickers hardness of the stir zone in copper nanopowder alloyed Al7075 T651 was increased by 20% compared to that of the heat affected zone, while the as-FSPed samples did not show a noticeable increase in hardness in the same zone. X-ray mapping showed traces of copper nanopowder after the process, and TEM was used to verify if there is CuAl2 formed in the copper alloyed sample.

5:10 PM

The Model of Structure Refinement in Metals at Large Deformations and Factors Effecting Grain Sizes: *Farid Utyashev*[1]; Georgy Raab[2]; [1]Institute for Metals Superplasticity Problems of the Russian Academy of Sciences; [2]Ufa State Aviation Technical University

The present work considers the essence of fragmentation: on the level of a simple model as a material response to the curvature accumulated by it at large deformations. It is on this basis that the correlation between curvature and fragment sizes is determined. It is shown that at deformation the area of curvature center inevitably changes. It is revealed that a specific value of variation of center surface area, i.e. ΔAY parameter, is numerically equal to the value of curvature acquired by a material. Minimum sizes of fragments and grains depending on ΔAY have been estimated, and the dependence of this parameter on strain has been established. Besides, the present paper considers the effects exerted by curvature center geometry, material distortion, directions of deformation and thermal warming up in the localization zones on structure refinement when various techniques are applied.

Multicomponent-Multiphase Diffusion Symposium in Honor of Mysore A. Dayananda: Modeling and Simulation

Sponsored by: The Minerals, Metals and Materials Society, ASM Materials Science Critical Technology Sector, ASM-MSCTS: Atomic Transport Committee

Program Organizers: Yong-Ho Sohn, University of Central Florida; Carelyn E. Campbell, National Institute of Standards and Technology; Richard Dean Sisson, Worcester Polytechnic Institute; John E. Morrall, Ohio State University

Monday PM
March 13, 2006

Room: 203B
Location: Henry B. Gonzalez Convention Ctr.

Session Chairs: John Agren, Royal Institute of Technology; Irena V. Belova, University of Newcastle

2:00 PM Invited

Phase Field Modeling of Interdiffusion Microstructures: *Yunzhi Wang*[1]; John E. Morrall[1]; [1]Ohio State University

One of the many outstanding contributions of Professor Dayananda to multicomponent-multiphase diffusion is his systematic experimental characterization of complex interdiffusion microstructures. These observations have posed serious challenges to existing theories and models and offered vast opportunities for new scientific discoveries. With the increasing power

of computers and sophistication of computational models, new understanding of the scientific principles underlying multicomponent diffusion in multiphase systems are anticipated. In this presentation we will review recent applications of the phase field method to studying interdiffusion microstructures and diffusion paths in multicomponent and multiphase systems. In particular, the phenomenon of demixing and the formation of non-linear diffusion paths with "horns" in two-phase/two-phase diffusion couples will be analyzed. Also the influence of the Kirkendall effect on interdiffusion microstructures and diffusion paths will be addressed. Whenever possible, the phase field simulations will be compared with DICTRA simulations and experimental observations.

2:30 PM

Modeling Diffusion in the Multicomponent Ordered $L1_2$ and B2 Phases for Ni-Rich Systems: *Carelyn E. Campbell*[1]; [1]National Institute of Standards and Technology

Modeling the diffusion in multicomponent ordered phases ($L1_2$ and B2) in Ni-base superalloys is essential for diffusion simulations that predict microstructure evolution. The ordered $L1_2$ (γ') phase is the primary strengthening precipitate for these alloys and the $L1_2$ phase fraction often exceeds 0.5. The ordered B2 phase is the primary component of many of the bond coats used to prevent diffusion between the thermal barrier coating and the superalloy. The ordered diffusion model proposed by Helander and Ågren (1999) is implemented for the $L1_2$ and B2 phases in the Ni-based superalloys. A new assessment for the Ni-Al $L1_2$ phase is presented. The diffusion mobilities for the B2 Ni-Al phase are re-assessed based on new experimental work by Kim and Chang (2000). The models employed in the assessments are evaluated by comparing measured and calculated composition profiles of various superalloys versus B2-NiAl diffusion couples.

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Modeling of Kinetics of Diffusive Phase Transformation in Binary Systems with Multiple Stoichiometric Phases: *Ernst Kozeschnik*[1]; Jiri Svoboda[2]; Franz D. Fischer[3]; [1]Graz University of Technology; [2]Academy of Sciences of the Czech Republic; [3]University of Leoben

Kirkendall experiments were performed on systems forming manifold nearly stoichiometric phases demonstrating, that the originally single Kirkendall plane is split into several planes. Such problem cannot be simply treated as a reactive diffusion problem and must be investigated as a transformation problem with active sources and sinks for vacancies at mobile interfaces between individual phases. The chemically driven strain must also be involved. The thermodynamic extremal principle is used for the treatment of the evolution of the binary system under the assumption that all phases existing in the system are stoichiometric with no sources and sinks for vacancies in the bulk. Furthermore, it is assumed that more than one phase nucleate at the contact plane of the diffusion couple at the start of the experiment. Then it is shown, that just the number of the nucleated phases determines the number of furcations of the Kirkendall plane.

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Phase-Field Simulation of Microstructural Evolution in Ternary Multiphase Diffusion Couples: *Rashmi R. Mohanty*[1]; Yong-Ho Sohn[1]; [1]University of Central Florida

A ternary phase-field model was devised and applied to examine the evolution of microstructure in multiphase solid-to-solid diffusion couples. Numerical model based on the Cahn-Hilliard and Ginzburg-Landau equations for multicomponent system were employed. The free energy of the system was derived based on the available thermodynamic data from the literature. The chemical mobility was varied as a function of composition from constant atomic mobility for a component as a first approximation. Effect of composition and perturbation on the development of planar and non-planar interfaces in multiphase diffusion couples was studied. Simulation results were compared with the experimental observations reported in literature for selected ternary systems. This work was financially supported by CAREER award from National Science Foundation (DMR-0238356).

3:45 PM Break

4:05 PM Invited

Comparison of Multicomponent Diffusion Programs: *Martin E. Glicksman*[1]; Afina Lupulescu[1]; Ben Pletcher[1]; [1]Rensselaer Polytechnic Institute

Currently three diffusion programs are in use for predicting concentration profiles of multicomponent couples: Profiler©, MultiDiflux©, DICTRA©. Each is unique in its incorporation of fundamental principles and capabilities, with the common goal of analysis of multicomponent diffusion data. Profiler© is useful when the diffusion is linear, and the interdiffusion coefficients or thermodynamic data are known. MultiDiflux© is capable of determining interdiffusion coefficients for multicomponent couples. However, accurate experimental penetration data are required to accommodate the interpolation scheme used by the numerical methods. DICTRA© is a program that accurately models experimental data from thermodynamic and kinetic coefficients. DICTRA© produces both interdiffusion and self-diffusiviion coefficients. Its use is limited by the accuracy and completeness of the associated data base. Comparison of all 3 software outputs will be presented for Fe-Al–Cr ternary diffusion couples. Experimental data used in our comparison were kindly provided by Professor Gunter Borchardt and Dr. Patrick Dawah.

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Diffusion Phenomena in the Planck-Kleinert Crystal: *Marek Danielewski*[1]; [1]AGH University of Science and Technology

The Planck-Kleinert Crystal (PKC) hypothesis is the promising area of Planck scale physics. In such quasi-continuum the energy, momentum and mass transport are diffusion controlled and all fluxes are given by the Nernst-Planck formulae. PKC hypothesis is used here to show the complexity of transport phenomena in cubic crystal. The quasi-stationary collective behavior of particles in the PKC (wave) is equivalent to the body (particle) and such an approach enables the Schrödinger equation to be derived. Transverse wave is equivalent electromagnetic wave. The diffusing interstitial particles create the gravitational type interaction between bodies. Thus, the PKC model implies four different force fields and predicts the vast amount of the "dark matter and dark energy" in the PKC. Apart from its fundamental impact on cosmology and physics, the Planck-Kleinert-Crystal model shows the exciting new possibilities in area of materials science, chemistry and physics of solids.

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MATLAB© Implementation of Diffusion Methods: Afina Lupulescu[1]; Christopher O'Brien[1]; *Martin Eden Glicksman*[1]; Wei Yang[1]; [1]Rensselaer Polytechnic Institute

We developed a MATLAB© code called Inversemethods© to determine concentration–dependent diffusivities from binary penetration data. Inversemethods© allows comparison between diffusivities calculated by five methods: 1) Boltzmann-Matano (BM); 2) Sauer-Freise/den Broeder (SFB); 3) Fictitious image–sources (error function approximation); 4) Fourier series image–sources, and 5) Linear diffusion couple (Grube-Jedele). Writing this code in MATLAB© met the requirement for portability, as MATLAB© is multi-platform enabling users to perform analyses on the diffusivity data produced with it. The BM and SFB methods are implemented following Simpson's rule to calculate the integrals, and employ a straightforward finite–difference method to estimate derivatives. The software also implements a Savizky-Golay filtering algorithm to smooth noisy penetration data by locally fitting a 3rd-order polynomial to 201 concentration-distance data points. A separate GUI has been developed by one of us to obviate the direct use of the MATLAB© code itself, and to ease its application for inexperienced users.

Point Defects in Materials: Mechanical and Boundary Properties

Sponsored by: The Minerals, Metals and Materials Society, TMS Electronic, Magnetic, and Photonic Materials Division, TMS Structural Materials Division, TMS: Chemistry and Physics of Materials Committee
Program Organizers: Dallas R. Trinkle, U.S. Air Force; Yuri Mishin, George Mason University; David N. Seidman, Northwestern University; David J. Srolovitz, Princeton University

Monday PM Room: 210B
March 13, 2006 Location: Henry B. Gonzalez Convention Ctr.

Session Chair: Yuri Mishin, George Mason University

2:00 PM Invited
The Influence of Interstitial Oxygen on the Alpha to Omega Phase Transition in Titanium and Zirconium: *Ellen K. Cerreta*[1]; George T. Gray[1]; Angus C. Lawson[1]; Chuck E. Morris[1]; Robert S. Hixson[1]; Paulo A. Rigg[1]; [1]Los Alamos National Laboratory

The pressure for the alpha to omega phase transition was investigated for two grades of titanium and three grades of zirconium. A series of shock experiments were conducted from 5 to 35GPa and revealed that the pressure for the phase transition increases with increasing interstitial oxygen content and is completely suppressed in low purity materials. For the high purity Ti and Zr in this study, the pressure for the phase transition occurred at 10.4 and 7.1GPa, respectively and no reverse transformation was observed upon unloading. Increasing the oxygen content increases the number of octahedral sites occupied; this is postulated to increase the pressure for the phase transition. Neutron diffraction and TEM were utilized to quantify the volume fraction of metastable omega phase and to characterize the microstructures within the shocked and "soft" recovered specimens. Quasi-static reload experiments examined the effect of the shock-induced substructure on post-shock mechanical properties.

2:30 PM
Solid Solution Softening in Mo Alloys: Large-Scale Model with Ab-Initio Parametrization: *Yuri N. Gornostyrev*[1]; Nadezhda I. Medvedeva[2]; Arthur J. Freeman[1]; [1]Northwestern University; [2]Institute of Solid State Chemistry

The intrinsic mechanism of solid solution softening (SSS) in bcc molybdenum alloys due to transition metal additions is investigated on the basis of *ab-initio* electronic-structure calculations. We demonstrate that additions with an excess of electrons lead to a decrease in the atomic row displacement and generalized stacking fault (GSF) energies, and those with a lack of electrons to its sharp increase. Using the atomic row model, we show that (i) the isotropic core of the screw dislocation in Mo tends to change into a planar core under alloying with softener solutes (Re, Os, Ir, Pt), and (ii) the decrease in GSF energy leads to the enhancement of double kink nucleation and dislocation mobility. Our study explains the experimental dependence of the alloying effect on the atomic number of the addition and provides an understanding of the electronic reasons for SSS in Mo. Supported by the AFOSR (grant No. FA9550-04-1-0013).

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New Quantitative Analysis Explains Softening of Pure Metals by Solutes: *Dallas R. Trinkle*[1]; Christopher F. Woodward[1]; [1]U.S. Air Force

Solid solution softening observed in bcc transition metals has traditionally been attributed to either extrinsic effects—such as interstitial scavanging—or intrinsic effects—direct solute/dislocation interaction. We investigate intrinsic mechanisms using first principles methods. First, density functional theory calculates directly the interaction energy of Hf, Ta, Re, Os, Ir and Pt solutes with a single straight <111> screw dislocation in Mo. Next, the interaction energies and changes in resistance to dislocation motion are incorporated into a mesoscopic double-kink model to predict changes in yield stress with temperature and solute concentration. Quantitatively accurate predictions require a model that accounts for clusters of solutes interacting with dislocations. Moreover, using the solute response in bulk as an approximation to the solute response in a dislocation can lead to incorrect predictions. By using solute-dislocation interactions coupled with a realistic mesoscopic model, we reproduce the strength behavior of Mo-Re and Mo-Pt, two systems with dramatically different intrinsic softening.

3:10 PM Invited
Role of Evolving Solute Structures on the Mechanical Behavior of Solid Solutions: *Catalin Picu*[1]; [1]Rensselaer Polytechnic Institute

An experimental and combined atomistic, mesoscale and continuum modeling program was developed to investigate the influence of evolving solute structures on the mechanical response of solid solutions. By solute structures we understand clusters located at and away from dislocations, and nanoscale precipitates composed of several solute atoms. We focus on the Al-5%Mg binary alloy, which we take as a model system. The rate sensitivity of this material decreases as the solute concentration increases. The current mechanisms proposed to explain this phenomenon are discussed in light of the new findings. Specifically, we study bulk and pipe diffusion to dislocation cores looking for the size and structure of stable clusters, and the characteristic time of their growth. Several new effects that lead to negative rate sensitivity will be presented and discussed against previously proposed mechanisms.

3:40 PM Break

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The Effect of Oxygen Vacancy on Mechanical Properties of Ceria: *Fereshteh Ebrahimi*[1]; Yanli Wang[1]; Keith L. Duncan[1]; Eric D. Wachsman[1]; [1]University of Florida

High concentrations of oxygen vacancies were produced by heat treating ceria at an elevated temperature in various environments with different partial pressures of oxygen, followed by fast cooling to room temperature. The elastic modulus, hardness and fracture toughness were evaluated at room temperature. The results indicate that the intrinsic elastic modulus decreases with increasing the oxygen vacancy concentration, consistent with theoretical predictions. However, hardness and toughness exhibited different relationships with the defect content. Several phenomena, including phase transformation, internal stress gradient, and microcracking, were found as a result of the applied heat treatments. These observations will be discussed and correlated with the variations in mechanical properties as a function of partial pressure of oxygen. The financial support by DOE under contract DE-PS26-02NT41562 for conducting this research is greatly appreciated.

4:15 PM
Study of Defect Structures in B2 Phases via First-Principles Calculations: *Sara N. Prins*[1]; Raymundo Arroyave[1]; Zi-Kui Liu[1]; [1]Pennsylvania State University

The B2 aluminides of Ir, Ni, Pd, Pt, and Ru are studied for their potential application as high temperature structural materials in the bond coats in turbine jet engines. It is well known that the mechanical properties of B2 intermetallic phases are controlled by their defect structures, e.g. the hardness of NiAl is attributed to the presence of vacancies. Thus to optimise the properties of a B2 phase, its defect structures and the effect of alloying additions should be well understood. In the present work, first-principles methods are employed to investigate the defect structure in B2 aluminides as well as the energy of formation of defects through the Wagner-Schottky and Bragg-Williams models.

4:35 PM Invited
Doped Metal Grain Boundaries: *Gerd Duscher*[1]; Wolfgang Windl[2]; Matthew F. Chisholm[3]; [1]North Carolina State University/Oak Ridge National Laboratory; [2]Ohio State University; [3]Oak Ridge National Laboratory

The combination of atomic-column resolved Z-contrast imaging, spatially resolved electron energy loss spectroscopy and *ab initio* density functional theory is used to study the atomic structure of doped metal grain boundaries. We will discuss three different materials (Al, Cu, and Ni_3Al), in which the atomic structure of tilt grain boudanries is very similar. We dope these grain boundary with intersititial (Cu in Al and B in Ni_3Al) and substitutional (Bi in Cu) segregants. The changes in the electronic structure are discussed in terms of bond strength. Strained supercells allow the determination of stress concentration on specific atomic sites. We also

will present results of point defect diffusion along Cu doped Al grain boundaries. Our findings suggest a new concept for the determination of grain boundary embrittlement.

5:05 PM Invited
First Principles Calculations of Interfacial Boundaries in Ni-Ni3Al and Al-Al3Sc: *Christopher F. Woodward*[1]; Axel van De Walle[2]; Mark Asta[2]; [1]U.S. Air Force; [2]Northwestern University

Solute and precipitation strengthening are often used to optimize the properties of structural materials used in aerospace applications. A great deal can be learned about these alloys by studying the model binary and ternary systems. Here Ni-Ni3Al and Al-Al3Sc are used as model systems for the Ni-based superalloys and Sc strengthened Al alloys in order to estimate interfacial boundaries (IFB) properties. The thermodynamic properties of these IFB's strongly influence growth and coarsening rates of precipitates and are used in models of precipitation strengthening and microstructural evolution. Cluster expansion methods and lattice gas methods are used to study composition profiles and free energies of IFB's in these materials. In Al-Al3Sc a lattice gas model is used to predict Mg impurity segregation to the Al side of the (100) IFB. This result has recently been verified by atom probe tomography.

Solidification Modelling and Microstructure Formation: A Symposium in Honor of Prof. John Hunt: Dendritic Growth II

Sponsored by: The Minerals, Metals and Materials Society, TMS Materials Processing and Manufacturing Division, TMS: Solidification Committee
Program Organizers: D. Graham McCartney, University of Nottingham; Peter D. Lee, Imperial College; Qingyou Han, Oak Ridge National Laboratory

Monday PM Room: 6C
March 13, 2006 Location: Henry B. Gonzalez Convention Ctr.

Session Chairs: H. Jones, University of Sheffield; C. Beckermann, University of Iowa

2:00 PM Invited
Dendritic Growth and Melting: *Martin E. Glicksman*[1]; Afina Lupulescu[1]; Matthew Koss[2]; [1]Rensselaer Polytechnic Institute; [2]College of the Holy Cross

Measurements of video data on melting dendritic fragments in reduced gravity show that the axial ratio of these needle-shaped crystals, C/A, initially rises until the crystal melts to a pole-to-pole length of ~5mm. At that point a sudden fall in the C/A ratio occurs. Analysis and modeling show that the cause of these sudden changes in kinetics and morphology during melting is the shape anisotropy of the fragments. Shape anisotropy leads to steep gradients in the mean curvature of the solid-melt interface, and, acting through the Gibbs-Thomson effect, induce unusual fluxes of heat within the crystallites. When the additional anisotropy of the interfacial free energy is added, a startling result obtains: the Gibbs-Thomson effect becomes non-monotonic! The poles are slightly warmer than the near-polar regions. This non-monotonic boundary condition might provide the physical basis for a dendritic limit cycle and account for the formation of dendritic side branching.

2:25 PM Invited
Formation of Globular Crystals during Semi-Solid Processing: *Weidong Huang*[1]; [1]Northwestern Polytechnical University

Both experimental and theoretical researches on the formation mechanism of the globular microstructure formed during semi-solid processing of a binary alloy were carried out, with focus on the strong convection effect induced by the forced melt stirring during the processing. Direct observation of the crystal growth from a transparent model alloy, succinonitrile-5at%water, during semi-solid processing indicates that strong melt convection induced by the forced stirring during semi-solid processing will change the crystal growth morphology from dendritical to spherical shape. This morphology change does not originate from dendrite arm fragmentation, instead from the increase of the interfacial morphological stability. An interfacial morphological stability analysis of a growing globular crystal indicates that the liquid convection and multi-particle effect will increase the critical radius for stable growth of the crystals.

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Characteristic Evaluation of Semi-Solid Aluminum Alloys Using Electromagnetic Stirring: Dock-Young Lee[1]; *Ki-Bae Kim*[1]; Jung-Hwa Mun[1]; Suk-Won Kang[1]; Seung-Kwon Seol[2]; Jung-Ho Je[2]; Do-Hyang Kim[3]; [1]Korea Institute of Science and Technology; [2]Pohang University of Science and Technology; [3]Yonsei University

Coherent X-rays from synchrotron beam sources are increasingly used in non-conventional techniques. This study presents three dimension microstructural characterization by synchrotron X-ray tomography of Al-15%Cu alloys. Qualitative results concerning the evolution of the shape of the globules and quantitative three dimension image analyses are presented. The microstructure of the solidified specimen was characterized as a size and shape of primary crystal in accordance with the flow density. By using three dimension synchrotron X-ray tomography, three dimension image of primary crystal was pictured and showed that the dendritic primary crystal was truncated due to the electromagnetic stirring during solidification. In this study synchrotron X-ray tomography appears as a very powerful tool for characterizing the microstructure of Al-15%Cu samples during partial solidification. The advantage of Al-15%Cu alloys lies in the possible use of the refraction and absorption mode for the synchrotron X-rays tomography.

3:15 PM
A Solid Fraction Evolution Approach for Modeling of Dendritic Growth in Multicomponent Alloys: *Adrian V. Catalina*[1]; Doru M. Stefanescu[2]; Leo Chuzhoy[1]; Michael L. Johnson[1]; [1]Caterpillar Inc.; [2]Ohio State University

A deterministic model that outputs microstructure images has been developed to simulate microstructure evolution during solidification of single phase multicomponent alloys. The model accounts for nucleation, growth, and coarsening of grains as well as redistribution/segregation of alloying elements during solidification. The model describes the grain growth by means of a strong coupling between the thermal and solutal fields at the solid/liquid interface. This novel coupling procedure allows relaxing the assumption used in previously published models that growth is controlled mainly by solute diffusion, which limits their validity to low cooling rates and growth velocities. Also, the new model can accommodate any number of alloying/impurity elements, including pure metals, in the chemical composition of the melt and account for their effect on the grain growth rate. Computed dendritic microstructures and segregation patterns will be presented for steels of various chemical compositions. Model validation against available literature data will also be discussed.

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3:55 PM Invited
Modeling of Single Cell/Dendrite Growth in Directional Solidification: *Shu-Zu Lu*[1]; Shan Liu[2]; [1]Michigan Technology University; [2]Ames Laboratory

Following the original model of single cell/dendrite growth in directional solidification by Hunt, in which it is assumed that there is no mass transfer cross the boundary walls, computation is carried out in focus on the selection of the tip shape as well as the tip undercooling and the tip radius. The solutions of cell/dendrite shapes are compared with the results of experimental modeling of single cell/dendrite growth in fine capillary tubes of 75 mm and 100 mm in diameter for Succinonitril- Salol system. The effects of the system constants on the single cell/dendrite growth are discussed and it is noticed that surface energy anisotropy has a significant effect on controlling cell/ dendrite shapes.

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Phase-Field Study of the Cellular Bifurcation in Dilute Binary Alloys: *Mathis O. Plapp*[1]; Esteban Meca[2]; [1]Ecole Polytechnique, Palaiseau; [2]Universitat Politecnica de Catalunya

Phase-field simulations in both two and three dimensions are used to investigate the microstructures which form closely above the threshold of

the Mullins-Sekerka instability in the directional solidification of dilute binary alloys. In particular, the so-called 'node' or 'pox' structures, which consist of regular hexagonal arrays of 'holes' (local depressions of the solidification front), are studied, and their properties are compared to the ones of the well-known hexagonal cell patterns. The results are compared to the predictions of weakly nonlinear amplitude expansions and to experimental data, and the implications of these findings for the selection of the microstructure spacing in extended systems are discussed.

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The Influence of Fluid Flow on the Microstructure of Directionally Solidified AlSi-Base Alloys: *Sonja Steinbach*[1]; Lorenz Ratke[1]; [1]German Aerospace Center DLR

To obtain a quantitative understanding of the effect of fluid flow on the microstructure of cast alloys a technical Al-Si-Mg alloy (A357) has been directionally solidified with medium temperature gradient under well defined thermal and fluid flow conditions. The solidification was studied in an aerogel-based furnace inducing flat isotherms and allowing the direct optical observation of the solidification process. Three pairs of Helmholtz coils around the sample induce a homogeneous rotating magnetic field (RMF) and hence a well defined flow field. The application of RMFs during directional solidification results in pronounced segregation effects: a change to pure eutectic solidification at the axis of the sample is observed at high magnetic field strengths. Microstructural features like the primary dendrite stem and secondary dendrite arm spacing change in a unique manner with solidification speed and magnetic field induction. In addition the arrangement of intermetallics can be modified with RMF induced fluid flow.

Space Reactor Fuels and Materials: Environmental Effects and Fuels

Sponsored by: The Minerals, Metals and Materials Society, ASM International, TMS Structural Materials Division, TMS/ASM: Nuclear Materials Committee, TMS: Refractory Metals Committee
Program Organizers: David James Senor, Pacific Northwest National Laboratory; Brian D. Wirth, University of California; Robert Hanrahan, Los Alamos National Laboratory; Steven J. Zinkle, Oak Ridge National Laboratory; Mehmet Uz, Lafayette College; Evan K. Ohriner, Oak Ridge National Laboratory; Brian V. Cockeram, Bechtel Bettis Inc

Monday PM
March 13, 2006

Room: 213B
Location: Henry B. Gonzalez Convention Ctr.

Session Chairs: Mehmet Uz, Lafayette College; Steven J. Zinkle, Oak Ridge National Laboratory

2:00 PM

Aging Effects on Microstructural and Mechanical Properties of Select Refractory Alloys for Space Reactor Applications: *Keith John Leonard*[1]; Jeremy T. Busby[1]; Steven J. Zinkle[1]; Rita Baranwal[2]; T. Angeliu[3]; Y. Ballout[3]; [1]Oak Ridge National Laboratory; [2]Bechtel Bettis Inc; [3]Lockheed Martin Corporation

Refractory alloys based on niobium, tantalum and molybdenum are potential candidate materials for structural applications in proposed space nuclear reactors. Long-term microstructural stability is a requirement of these materials for their use in this type of creep dominated application. Early work on refractory alloys has shown aging embrittlement occurring for some niobium and tantalum-base alloys at temperatures near 40% of their melting temperatures in either the base metal or in weldments. Other work has suggested microstructural instabilities during long-term creep testing leading to decreased creep performance. This paper examines the effect of aging 1,000 hours at 825, 975 and 1125°C on the microstructural and mechanical properties of two niobium (Nb-1Zr and FS-85), tantalum (T-111 and ASTAR811C) and molybdenum (Mo-41Re and Mo-47.5Re) base alloys. Changes in material property are examined through mechanical tensile testing coupled with electrical resistivity changes and microstructural examination through optical and electron microscopy analysis. This work was performed in part by the Oak Ridge National Laboratory for the U.S. Department of Energy (DOE) in support of the National Aeronautics and Space Administration (NASA). ORNL is managed for DOE by UT-Battelle, LLC, under contract DE-AC-05-00OR22725. Any opinions expressed in this paper are those of the author(s) and do not necessarily reflect the views of DOE or NASA.

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Radiation-Damage in Molybdenum-Rhenium Alloys for Space Reactor Applications: *Jeremy T. Busby*[1]; Keith John Leonard[1]; Lance Snead[1]; F. W. Wiffen[1]; Steven J. Zinkle[1]; E. Mader[2]; R. Nelson[3]; George A. Newsome[3]; [1]Oak Ridge National Laboratory; [2]Bechtel-Bettis Inc; [3]Lockheed Martin

Various Mo-Re alloys are attractive candidates for use as fuel cladding and core structural materials in spacecraft reactor applications. Molybdenum alloys with rhenium contents of 41% to 47.5% (wt%), in particular, have good creep resistance and ductility in both base metal and weldments. However, irradiation-induced changes such as transmutation and radiation-induced segregation could lead to precipitation and, ultimately, radiation-induced embrittlement. This paper presents the characterization of radiation-induced changes in two Mo-Re alloys. Results from Mo-41Re and Mo-47.5Re alloys irradiated to ~ 1 and 2 dpa at 800, 950, and 1100°C in the High Flux Isotope Reactor at Oak Ridge National Laboratory are presented. The impact of irradiation on electrical resistivity and swelling will be assessed. Transmission-electron microscopy analysis will be used to examine radiation-induced segregation of Re, transmutation of Re to Os, and any precipitation resulting from these composition changes. The impact of these irradiation-induced changes on mechanical properties will be discussed. This work was performed in part by the Oak Ridge National Laboratory for the U.S. Department of Energy (DOE) in support of the National Aeronautics and Space Administration (NASA). ORNL is managed for DOE by UT-Battelle, LLC, under contract DE-AC-05-00OR22725. Any opinions expressed in this paper are those of the author(s) and do not necessarily reflect the views of DOE or NASA.

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The Swelling, Microstructure, and Hardening of Wrought LCAC, TZM, and ODS Molybdenum Following Neutron Irradiation: *Brian Vern Cockeram*[1]; Rita Baranwal[1]; Richard W. Smith[1]; Nao Hoshimoto[2]; Lance L. Snead[2]; [1]Bechtel-Bettis; [2]Oak Ridge National Laboratory

Molybdenum can be susceptible to embrittlement after neutron irradiation at temperatures <800°C. In this work, TEM examiantions are used to characterize wrought Low Carbon Arc Cast, ODS, and TZM molybdenum following irradiation in HFIR at 300°C, 600°C, and 870-1100°C. The size and number density of loops and voids are determined. Models for the increase in strength are evalauted by comparing measured tensile strength values from previous work to values that are predicted using the microstructural data. Irradiation of alloys at 300C results in the formation of a high number density of the fine loops and voids (about 1-3 nm). A relatively high number density of small voids (about 5-6 nm) are observed after irradiation at 600°C. A low number density of coarse voids (about 10-20 nm) are observed after irradiation at 870-1100°C. Swelling values obtained from density measurements are consistent with the microstructure data. The evolution of microstructure is discussed.

3:15 PM Break

3:30 PM

Literature Review of W-UO_2 Cermet Thermal and Radiation Performance: *Robert J. Hanrahan*[1]; Carol L. Haertling[1]; [1]Los Alamos National Laboratory

At minimum, the fuel used in nuclear thermal propulsion reactors must have high-temperature stability and strength and be compatible with hydrogen. The fuel should also retain fissile material and fission products and be stable under thermal cycling. Candidate materials are therefore limited to nuclear materials in the form of or combined with ceramics (oxides, carbides, and nitrides), refractory metals, and graphite. To date, no ideal material has been identified, but ceramic metal composites (cermets) have long been considered as potential fuel materials. Although graphite matrix materials were used in the Rover and NERVA programs, the utility of cermets was studied extensively during the 1960s and early 1970s. The most-investigated fuels were UO_2 in a matrix of tungsten, molybdenum, or alloys thereof. The W-UO_2 system proved to be the most

promising for nuclear thermal propulsion. This presentation will review the thermal stability and irradiation performance of W- UO_2 cermets.

3:55 PM
Mechanical Properties and Microstructure of ZrN Pellets as Surrogates for Nitride Fuels: Effect of Sintering Conditions: Kirk Wheeler[1]; Manuel Parra[1]; John Dunwoody[2]; Darrin Byler[2]; *Pedro D. Peralta*[1]; Ken McClellan[2]; [1]Arizona State University; [2]Los Alamos National Laboratory

In this work, ZrN was studied as a diluent in non-fertile nitride transmutation fuel and as a surrogate to actinide nitrides such as PuN. The microstructure and mechanical properties at room temperature of sintered ZrN pellets were examined to investigate the effects of processing conditions on the structural integrity of fuel pellets. Powder size, mechanical milling, sintering temperature and atmosphere (Ar or N) were varied to form a matrix of conditions. The microstructure of the resulting pellets was examined using optical and electron microscopy and orientation imaging microscopy. Pore size and shape distributions were obtained from the measurements as well as crystallographic texture. Mechanical properties including hardness, fracture toughness and compression strength were measured at room temperature and correlated to microstructure and processing conditions. This, in turn, will lead the optimum processing parameters for manufacturing of actinide nitrides suitable for a variety of applications, including transmutation and space fuels.

4:20 PM
Kinetics of Precipitation of U_4O_9 from Hyper-Stoichiometric UO_{2+x}: *Sven Vogel*[1]; Sheldon White[2]; Jamie Higgs[2]; William T. Thompson[2]; [1]Los Alamos National Laboratory; [2]Royal Military College of Canada

For safe and reliable operation of fission reactors in space, the phase diagrams and reaction kinetics of systems used as nuclear fuels, such as U-O, U-N, U-C, are required. Diffraction allows identification of phases and their weight fractions as a function of temperature in situ, with a time resolution of the order of minutes. In this presentation, we will provide results from a neutron diffraction experiment validating the U-O system. Using the neutron diffractometer HIPPO, we investigated the decomposition of UO_{2+x} into UO_2 and U_4O_9 as a function of temperature in situ. From the diffraction data, the participating phases could be identified as UO_{2+x}, UO_2 and $U_4O_{8.936}$ and no stoichiometric U_4O_9 was found. We will also report results on similar experiments in the U-Dy-O system. Results of both experiments were used to improve existing thermodynamic and finite-element models. The presented technique is also applicable to the other systems mentioned above.

The Brandon Symposium: Advanced Materials and Characterization: Interfaces - Theory and Experiments

Sponsored by: The Minerals, Metals and Materials Society, Indian Institute of Metals, TMS Extraction and Processing Division, TMS: Materials Characterization Committee
Program Organizers: Srinivasa Ranganathan, Indian Institute of Science; Wayne D. Kaplan, Technion; Manfred R. Ruhle, Max-Planck Institute; David N. Seidman, Northwestern University; D. Shechtman, Technion; Tadao Watanabe, Tohoku University; Rachman Chaim, Technion

Monday PM
March 13, 2006
Room: 206B
Location: Henry B. Gonzalez Convention Ctr.

Session Chairs: Manfred Ruhle, MPI-Stuttgart; Rachman Chaim, Technion - Israel Institute of Technology

2:00 PM Invited
Exploring the Mechanical Response of Grain Boundaries: J. W. Cahn[1]; *Y. Mishin*[2]; A. Suzuki[2]; [1]National Institute of Standards and Technology; [2]George Mason University

The response of tilt grain boundaries (GBs) to applied shear stresses was investigated by means of molecular dynamics simulations performed over the entire misorientation range and a wide temperature range. Two fundamentally different types of response are found. At relatively low temperatures the stress induces GB motion accompanied by a coupled shear deformation in the volume traversed by the GB. The observed coupling depends on the tilt angle and is accurately described by a geometric model. The atomic mechanisms of the coupling have been identified and related to the GB crystallography. As the temperature increases, GB sliding events begin to occur until at higher temperatures the mechanical response switches entirely to sliding. The coupling/sliding crossover temperature range depends on the tilt angle. These findings suggest the need for a reinterpretation of many materialsphenomena, particularly grain growth, grain rotation, recrystallization, and plastic deformation of nanocrystalline materials.

2:25 PM Invited
Grain Boundary Transitions: *Ming Tang*[1]; W. Craig Carter[1]; Rowland Cannon[2]; [1]Massachusetts Institute of Technology; [2]Lawrence Berkeley National Laboratory

A phase field model that incorporates crystallographic orientation and grain boundary disorder has been developed. In fixed stoicheometric materials and binary alloys, we have analyzed the equilibrium properties of grain boundaries as a function of their misorientation using a diffuse interface model that depends on empirical molar free energies and gradient energy coefficients. A graphical construction, similar to that which J. Cahn used to predict surface segregration transitions in his Critical Wetting model (1977), predicts an order-disorder transitions akin to grain boundary melting. We have discovered a similar, but more complicated, thermodynamic construction for alloys which demonstrates the collective behavior or grain boundary disorder and segregation. We catalog the thermodynamic conditions where first and second order boundary transitions are possible and produce a diagrams that, similar to classical phase diagrams, indicateconditions of stability and coexistence of multiple grain boundary complexions.

2:50 PM
On the Features of Dislocation-Obstacle Interactions in Thin Films: Direct Comparison between In Situ Experiments and Large Scale Atomistic Simulations: *Yuri Osetsky*[1]; Yoshitaka Matsukawa[1]; Roger Stoller[1]; Steven Zinkle[1]; [1]Oak Ridge National Laboratory

Large-scale atomistic modelling has demonstrated that the dynamic interactions of dislocations in thin films have a number of remarkable features. A particular example is the interaction between a screw dislocation and a stacking fault tetrahedron (SFT) in Cu which can be directly compared with in situ observations of quenched or irradiated fcc metals. If the specimen is thin, the dislocation velocity is slow and the temperature is high enough, a segment of the original SFT can be transported towards the surface via a double cross-slip mechanism and fast glide of an edge dislocation segment formed during the interaction. The mechanisms observed in the simulations provide an explanation for the results of in situ straining experiments and the differences between bulk and thin film experiments. Research sponsored by the Division of Materials Sciences and Engineering and the Office of Fusion Energy Sciences, U.S. DOE, under contract DE-AC05-00OR22725 with UT-Battelle.

3:05 PM Invited
Atomistic Calculations of Microstructural Evolution in Shocked Nickel: *Srinivasan G. Srivilliputhur*[1]; M. I. Baskes[1]; [1]Los Alamos National Laboratory

Shock wave propagation in materials, and the attendant dislocation nucleation and motion, causes phase transformations and complex microstructure development. We present some atomistic calculations of these phenomena in single crystal nickel, a typical fcc metal. Following general observations about shock induced phase transformations at high strain rates and stress may be made: (1) the fcc crystal transforms to a bcc-like crystal behind the shock wave; (2) after a period of time, the bcc structure transforms to domains of a highly faulted fcc structure; (3) the domains grow, forming twin boundaries at their intersections; and (4) the reflected shock wave drives the system to a faulted, polycrystalline fcc material. While these observations appear to be insensitive to the in-plane sample periodicity, the details of fault and twin spacing scales are not. Understanding these microstructural features, and their scaling with system sizes, will help us bridge atomistic calculations with continuum scale experiments.

3:30 PM Invited

Building Carbon Nanotube Architectures for Applications: *Pulickel M. Ajayan*[1]; [1]Rensselaer Polytechnic Institute

The talk will focus on the recent developments in our laboratory on the fabrication of carbon nanotube based architectures tailored for various applications. Various organized architectures of multiwalled and singlewalled carbon nanotubes can be fabricated using relatively simple vapor deposition processes and the work in attaining control on the directed assembly of nanotubes will be highlighted. We have pursued several electrodes novel applications for these structures, for example, as nanostructured electrodes for gas breakdown sensors, horizontal and vertical electrical interconnects, unique filters for separation technologies, thermal management systems, multifunctional brushes, and polymer infiltrated thin film composites. Some of these promising applications of carbon nanotubes and composites will be reviewed from the perspective of what has been accomplished in recent years. Our efforts on the strategies of growth and manipulation of nanotube-based structures and our recent success in controllably fabricating hierarchically branched nanotube structures will be discussed.

3:55 PM Break

4:05 PM Invited

Stability of Heterophase Boundaries between Different Metals and Sapphire: *Manfred R. Ruhle*[1]; Elena Tchernychova[1]; Gunther Richter[1]; Sang Ho Oh[1]; Christina Scheu[1]; [1]Max-Planck Institute

Well defined interfaces between different single crystalline metals (M=Nb, Mo, Al,Ag,Cu)and specific sapphire surfaces (SP)were processed by molecular beam epitaxy (MBE) or high temperature diffusion bonding (HTDB). The structure, composition and bonding of the as-processed interfaces were determined over many length scales to the atomic level by advanced TEM techniques. The bonding across the interface depends on the nature of the SP surface. High density of oxygen ions at the outermost SP layer results in strong bonding across the interface. Post-processing annealing under well defined conditions (temperature), oxygen partial pressure; (pO_2) results in specific reaction products at the interface. These reaction products alter the properties of the interface. Results will be reported for the 5 M/SP systems and discussed on the basis of thermodynamic and kinetic considerations. As expected the interfaces between SP and metals are morphologically stable owing to the specific properties of SP.

4:30 PM Invited

Interfaces between Pb Grains and Cu Surfaces: *Dominique Chatain*[1]; Daniel Galy[2]; [1]Centre National de La Recherche Scientifique; [2]Synergie 4

We report on investigations of the interfaces between liquid or solid Pb and single- or poly-crystalline Cu substrates. EBSD analyses show that Pb grains have a different orientation relationship with Cu depending on whether Pb is deposited by PVD or solidified from droplets. When Pb is solidified from droplets, surprisingly, a cube-on-cube orientation relationship prevails between the Pb crystals and the substrate on each Cu grain surface, whatever its surface orientation, even though the lattice parameter of Pb is 1.37 times larger than that of Cu. SEM and AFM analyses show that during annealing of Pb droplets, ridges build up at the droplet-substrate triple lines, indicating that the interfaces evolve towards equilibrium by diffusion processes. We discuss these features in comparison with experiments and calculations performed on Pb nanocrystals embedded in Al, another fcc solid with a lattice parameter smaller than that of Pb.

4:55 PM Invited

Diffusion Reactions at Metal–Oxide Interfaces: The Effect of an Applied Electric Field: Yeonseop Yu[1]; Jeremy Mark[1]; *Frank Ernst*[1]; Thomas Wagner[2]; Gurpreet Singh[3]; Rishi Raj[3]; [1]CASE; [2]Max-Planck-Institut für Metallforschung; [3]University of Colorado

We have studied the effect of an applied electric field on diffusion reactions at Al—$MgAl_2O_4$ interfaces. Annealing experiments were carried out at 620°C with (i) no applied electric field, (ii) an applied electric field oriented towards the Al epilayer, and (iii) an applied electric field oriented towards the $MgAl_2O_4$ substrate. The resulting microstructural changes after different annealing times were investigated by advanced, complementary methods of transmission electron microscopy. Our studies reveal that an electric field oriented towards the MBE-grown Al layer promotes the growth of a Mg-deficient phase — presumably γ-Al_2O_3. A field in the opposite direction, in contrast, does not result in the formation of a reaction phase. A model will be presented to explain these observations, which may be significant for controling the mechanical properties of related metal—oxide interfaces.

5:20 PM Invited

Bonding and Interface Structures of Metal/SrTiO3 Systems: *Christina Scheu*[1]; Elena Tchernychova[2]; Klaus van Benthem[2]; Gunther Richter[2]; Thomas Wagner[2]; Manfred Rühle[2]; [1]University of Leoben; [2]Max-Planck-Institut für Metallforschung

In this study the interface structure of fcc and bcc metals deposited by molecular beam epitaxy on the (100) surface of single-crystalline SrTiO3 was investigated by high-resolution and analytical transmission electron microscopy. The interfaces are abrupt and, depending on the lattice mismatch, either coherent or semi-coherent interfaces form. Various orientation relationships were observed for the different metal/SrTiO3 interfaces. In all cases, the interfacial bonding involves metall-oxygen bonds as determined by energy-loss near-edge structure studies. The results indicate that Sr atoms do not participate in the adhesion and that the interfaces are terminated by TiO2 rather than SrO layers. In contrast, simulations of the high-resolution images indicate a slightly better agreement for SrO terminated models. The formation of the preferred orientation relationships and the interface features will be discussed based on geometrically constructed models and compared to theoretically predicted interface structures[1].[1]Ochs and Elsässer, Z. Metall. 5 (2002) 406.

The Rohatgi Honorary Symposium on Solidification Processing of Metal Matrix Composites: Processing and Microstructure of MMCs - I

Sponsored by: The Minerals, Metals and Materials Society, TMS Materials Processing and Manufacturing Division, TMS Structural Materials Division, TMS/ASM: Composite Materials Committee, TMS: Solidification Committee

Program Organizers: Nikhil Gupta, Polytechnic University; Warren H. Hunt, Aluminum Consultants Group Inc

Monday PM	Room: 207B
March 13, 2006	Location: Henry B. Gonzalez Convention Ctr.

Session Chairs: David J. Weiss, ECK Industries Inc; Doru M. Stefanescu, University of Alabama

2:00 PM Invited

Particle Interaction with the Solidification Front – A Fundamental, Multidisciplinary Problem: *Doru Michael Stefanescu*[1]; [1]Ohio State University

The interaction of particles with solid-liquid interfaces has been studied since the mid 1960's. While the original interest stemmed from geology applications (frost heaving in soil), researchers soon realized that understanding this phenomenon might yield practical benefits in other fields, including metallurgy and cryobiology. Significant research was focused on applications to metal matrix composites produced by casting or spray forming techniques. In the most common cast metal matrix composites, Al-Si/SiC particles, the particles are distributed at the grain boundaries, decreasing plastic properties. The particle-solid/liquid interface interaction was also found to play an important role in the solidification of ternary eutectics, in the formation of microporosity during solidification, and in the growing of 123 (YBaCu) superconductor crystals from an undercooled liquid.The paper will attempt to summarize the available experimental data for different applications. Then, it will review the main theoretical models discussing their strength and weaknesses in some detail.

2:25 PM Invited

Metal Matrix and Polymer Nanocomposites: *Rahul R. Maharsia*[1]; [1]Louisiana State University

Metal matrix composites (MMC) possess excellent thermal and mechanical properties and are widely used in aerospace and automobile applications. In this paper, the current state of research on nanoparticle filled MMCs is presented. Studies related particle packing, pushing and wetting are reviewed and mechanical properties of metal based nanocomposites are discussed. A comparison is made between material characteristics and properties of polymer matrix composites and MMCs modified through various nanoparticles.

2:50 PM Invited

The Technological Aspects of Alfa Composites Synthesis: Jerzy Sobczak[1]; Pawel Darlak[1]; Robert M. Purgert[2]; *Natalia Sobczak*[1]; Andrzej L. Wojcieszynski[3]; [1]Foundry Research Institute; [2]Energy Industries of Ohio; [3]Motor Transport Institute

Aluminum alloys containing fly ash (ALFA - Aluminum Fly Ash) composites have been developed in recent years. The use of fly ash as a filler or reinforcement for aluminum matrix composites is very desirable from an environmental standpoint. However, synthesis of ALFA composites by liquid phase routes is difficult due to poor wettability of fly ash by molten Al and Al alloys at industrially important temperatures and its lightweight nature (particularly for hollow spheres). In this work some technological aspects of ALFA composites synthesis have been discussed in order to demonstrate advantages and disadvantages of selected production methods as well as corresponding properties and possible applications of ALFA composites.

3:15 PM

The Influence of the Reinforcement Phase upon the Formation of Casting Defects in Aluminum Matrix - Al-Zr-O-B Particulate Composites: Richard W. Hamilton[1]; Yutao Zhao[2]; *Peter D. Lee*[1]; [1]Imperial College; [2]Jiangsu University

The presence of ceramic particles in cast materials at composite levels is well known to act as a reinforcing phase increasing final properties such as tensile and fatigue strength. However, well distributed particulate phases that are stable at melt temperature can also reduce the formation of casting defects such as porosity and segregation. A novel aluminium matrix composite reinforced with in-situ ZrB_2, Al_2O_3 and Al_3Zr particulates was synthesized using a magneto-chemical reaction in molten aluminium to produce a mixture of ZrB_2, $Al2O_3$ and Al_3Zr reinforcement particles. The influence of processing parameters on the reinforcement distribution, and the subsequent effect of the reinforcement on the resulting microstructure were investigated using in situ radiography, X-ray microtomography and standard characterisation techniques. The influence of volume fraction particulate on the distribution of porosity and segregation was quantified and reasons for the reduction in casting defects was hypothesised.

3:40 PM Invited

Solidification Rate Effects on Microstructural and Mechanical Properties in Pressure Cast Magnesium Metal Matrix Composites: *Adam Robert Loukus*[1]; [1]GS Engineering

Solidification rates play a large role in microstructural evolution in a cast component. Microstructures of cast composites add increased complexity to the solidification process due to the ceramic reinforcements (i.e. inclusions) cast into the component. Current observations suggest that the solidification rates have an impact on the grain size and structure in an MMC material. In the current study a pressure cast composite component is cast solidification rates are varied to study microstructural differences. The component is tensile tested and the grain size beneath the fracture surface is measured using SEM techniques. Effects of grain size, and intermetallic content in the cast component due to the various cooling rates are analyzed using a SEM machine while the macro effects are studied by testing elongation, ultimate strength and elastic modulus.

4:05 PM Break

4:20 PM

Fabrication of Carbon Fiber Reinforced Aluminum – Magnesium Alloy Composite Wires Using Ultrasonic Infiltration Method: *Tadashi Matsunaga*[1]; Kenji Ogata[1]; Tomei Hatamaya[1]; Kenji Shinozaki[1]; Makoto Yoshida[2]; [1]Hiroshima University; [2]Waseda University

M40J carbon fiber reinforced aluminum – 0, 1.3, 2.4, 4.7, 10 mass % magnesium alloy composite wires were fabricated by using ultrasonic infiltration method. Addition of magnesium into molten aluminum was remarkably improved infiltratability of the molten aluminum alloy into bundle of the carbon fiber regardless of fabricating speed from 0.03 to 0.22 m/s. In order to make clear the mechanism of infiltration of molten metal through the bundle using ultrasonic, the generating cavitations in the molten alloy were measured by means of acoustic emission. The cavitations were generated by addition of magnesium remarkably. As the results, the infiltratability strongly corresponded to the generating acoustic cavitation, which would be caused by addition of magnesium.

4:45 PM

Interaction between Molten Aluminum and Selected Oxides: *Natalia Sobczak*[1]; [1]Foundry Research Institute

In situ reactive synthesis of composite materials offers a number of advantages, of which the thermodynamic stability of reinforcing phases is the most important. Oxy-redox reactions between Al and reactive oxides have been successfully applied to synthesize Al-Al2O3 type composites having unique C4 structures by liquid phase processing using either vortex casting, reactive metal infiltration of porous ceramic preform or reactive metal penetration of dense ceramics. Whatever the process, the wettability and reactivity between Al and ceramic phase is required. The paper summarizes the experimental results on wettability and reactivity in different couples with simple oxide (Al/SiO2, Al/ZnO, Al/B6O, Al/TiO2, Al/ZrO2, Al/CoO, Al/NiO), binary oxides of SiO2-Al2O3 system and complex oxides of SiO2-Al2O3-Fe2O3-TiO2-CaO-MgO type. The analysis of factors affecting wetting and transformation kinetics in Al/reactive oxide couples has been done to demonstrate the possibility and to determine the conditions for in situ synthesis of composites materials by liquid phase route.

5:10 PM Invited

Processing and Characterization of Fly Ash Particle Reinforced A356 Al Composites: *Mirle Krishnegowda Surappa*[1]; Sudarshan[1]; [1]Indian Institute of Science

A356 Al - fly ash particle composites were fabricated using stir-cast technique. Bulk hardness and matrix microhardness of A356 Al-fly ash composites are higher compared to those of the unreinforced alloy. In the as extruded condition, 0.2% proof stress of the composites is higher compared to that of unreinforced alloy. Additions of fly ash leads to increase in hardness, elastic modulus and 0.2% proof stress. Composites reinforced with 12-volume % fly ash exhibits lower UTS compared to that of unreinforced alloy. The narrow size range fly ash particle reinforced composite shows better mechanical properties compare to wide size range particles. Damping behaviour of unreinforced alloy and their composites have been studied using dynamic mechanical thermal analyzer (DMTA). A356 Al-fly ash MMCs were found to exhibit improved damping capacity when compared to unreinforced alloy both at ambient temperatures and at elevated temperatures.

5:35 PM Invited

Fabrication and Microstructure of Magnesium Alloy- Fly Ash Microballoon Composites: *Atef Awad Doud*[1]; Pradeep Rohatgi[2]; [1]CMRDI; [2]University of Wisconsin-Madison

The ZC63 alloy- fly ash particles composite was processed by melt stir technique. Optical microscopy was used to reveal the microstructural features and the distribution of the fly ash particles. Compositional spot analyses were performed in and around the particles using an Energy Dispersive X-ray Analysis (EDXA) facility in the SEM. XRD analyses were carried out to identify the phases in the matrix alloy and composite. The density of the composites was determined using Archimedes‘ method, with ethanol as the suspending medium. Visual inspection of machined surface of the cast composite showed uniform distribution of fly ash microballoons throughout the casting. Casting defects were not noticed on the casting surface. The microstructure demonstrates even distribution of the particles in the Mg alloy matrix and there is no sign of fly ash cluster or residual porosity.

Titanium Alloys for High Temperature Applications - A Symposium Dedicated to the Memory of Dr. Martin Blackburn: Titanium Alloys for High Temperature Applications - In Memory of Dr. Martin Blackburn

Sponsored by: The Minerals, Metals and Materials Society, TMS Structural Materials Division, TMS: Titanium Committee
Program Organizers: Michael W. Peretti, Lyondell Chemical Company; Daniel Eylon, University of Dayton; Ulrike Habel, Munich; Guido C. Keijzers, Del West USA; Michael R. Winstone, DSTL

Monday PM — Room: 201
March 13, 2006 — Location: Henry B. Gonzalez Convention Ctr.

Session Chairs: James C. Williams, Ohio State University; Harry A. Lipsitt, Air Force Materials Laboratory, Retired

2:00 PM Introductory Comments

2:10 PM Keynote
Remembering Martin: Technical Contributor, Colleague and Friend: *James C. Williams*[1]; Harry A. Lipsitt[2]; Daniel F. Paulonis[3]; [1]Ohio State University; [2]Air Force Materials Laboratory, Retired; [3]Pratt & Whitney

This talk will outline some of the major technical contributions of Martin Blackburn, who truly was a pioneer in defining many aspects of the modern physical metallurgy and behavior of Ti alloys and of other structural alloys. It also will recall some of the wonderful wit and wisdom of this special person in (hopefully) a fun but respectful manner. The talk will comprise several distinct phases of Martin's professional life: The early Boeing years; the Air Force years and the Pratt & Whitney years.

Titanium Alloys for High Temperature Applications - A Symposium Dedicated to the Memory of Dr. Martin Blackburn: Applications of High Temperature Titanium Alloys

Sponsored by: The Minerals, Metals and Materials Society, TMS Structural Materials Division, TMS: Titanium Committee
Program Organizers: Michael W. Peretti, Lyondell Chemical Company; Daniel Eylon, University of Dayton; Ulrike Habel, Munich; Guido C. Keijzers, Del West USA; Michael R. Winstone, DSTL

Monday PM — Room: 201
March 13, 2006 — Location: Henry B. Gonzalez Convention Ctr.

Session Chairs: Michael W. Peretti, Lyondell Chemical Company; Michael R. Winstone, DSTL

3:00 PM Introductory Comments Address by Jack Schirra

3:10 PM Keynote
High Temperature Titanium Alloy Usage in Turbine Engines - Applications, Developments and Challenges: *John J. Schirra*[1]; Daniel F. Paulonis[1]; James O. Hansen[1]; Douglas Berczik[1]; [1]Pratt & Whitney

Titanium found ready acceptance in the aircraft engine industry with rapid growth in applications since its original implementation as compressor airfoils and fan disks in P&W J57 and JT3 engines. The specific strength capability of titanium was a key enabler to the development and widespread use of gas turbine engines. Titanium usage in commercial engines has plateaued at ~25% of system weight driven primarily by high temperature capability limitations including engineering capability and burn resistance. Due to system level requirements, titanium alloys, particularly burn resistant alloys, continued to find increased usage in military engines where weight requirements can balance the increased cost of these materials. This paper will review the history of titanium alloy usage at P&W, with a focus on advances made during Martin Blackburn's 25 year career in P&W Materials Laboratory, and highlight the application/development challenges required for continued significance of this material system to the engine community.

4:00 PM Break

4:30 PM Invited
High Temperature Titanium Alloy Applications at GE Aircraft Engines: *Andrew P. Woodfield*[1]; [1]GE Transportation

The current usage of high temperature titanium alloys within GE Aircraft Engines will be reviewed, highlighting issues associated with current and potential future alloys. In particular, the importance of understanding lower temperature phenomena such as dwell fatigue are key before introduction of new higher temperature titanium alloys.

5:00 PM Invited
Application of High Temperature Titanium Alloys in Aero-Engines - Limits Due to Bulk and Surface Related Properties: *Dietmar Helm*[1]; [1]MTU Aero Engines

This paper describes typical examples of the application of modern high temperature Titanium alloys as Ti 6242 and Timetal 834 in various sections of aero-engines. Specific attention is given to the relevance of optimized microstructures for best balances of required mechanical properties, weight optimization and surface integrity when being operated in air at temperatures exceeding 450°C. The example of Timetal 834, currently representing the alloy with the highest temperature capability being in service for major rotating parts and structural components, will be used to demonstrate the gap of maximum potential service temperature due to good bulk properties and thermodynamically stability and the limitation to lower service temperatures due to surface oxidation. The effects of protective coatings aiming for closing this gap will be discussed with relevance to mechanical properties. Furthermore, results of surface treatments as shot peening at high service temperatures will be presented.

Ultrafine Grained Materials - Fourth International Symposium: Processing and Microstructures I

Sponsored by: The Minerals, Metals and Materials Society, TMS Materials Processing and Manufacturing Division, TMS Structural Materials Division, TMS/ASM: Mechanical Behavior of Materials Committee, TMS: Shaping and Forming Committee
Program Organizers: Yuntian T. Zhu, Los Alamos National Laboratory; Terence G. Langdon, University of Southern California; Zenji Horita, Kyushu University; Michael Zehetbauer, University of Vienna; S. L. Semiatin, Air Force Research Laboratory; Terry C. Lowe, Los Alamos National Laboratory

Monday PM — Room: 217D
March 13, 2006 — Location: Henry B. Gonzalez Convention Ctr.

Session Chairs: Carl C. Koch, North Carolina State University; Ibrahim Karaman, Texas A&M University; S. L. Semiatin, Air Force Research Laboratory; Sergey Dobatkin, A.A. Baikov Institute of Metallurgy and Material Science

2:00 PM Invited
Artifact-Free Bulk Nanocrystalline Grain Size (< 100 Nm) Materials: The Processing Challenge: *Carl C. Koch*[1]; Khaled M. Youssef[1]; Ronald O. Scattergood[1]; Korukonda L. Murty[1]; [1]North Carolina State University

It has been clear for many years that bulk, artifact-free nanocrystalline materials are required for both meaningful mechanical testing and for potential structural applications. It is desirable to optimize strength by obtaining the smallest practical grain size - less than 50 nm if possible. A major challenge is to produce nanocrystalline materials with a fine grain size in bulk form without processing artifacts such as porosity, incomplete particulate bonding, or deleterious grain boundary impurities. In recent years progress in processing methods has allowed artifact-free metals and alloys to be made in bulk form. These materials can exhibit very high strength along with good ductility. The attractive processing techniques include special electro-deposition methods and certain severe plastic deformation methods. These advances in processing will be described in

this talk along with the results of mechanical tests on artifact-free materials. Future processing needs will be discussed.

2:20 PM Invited

Ductility Enhancement of Ultrafine Grained Commercially Pure 1050 Aluminum Alloy by Cross Accumulative Roll-Bonding (C-ARB): *Yong-Suk Kim*[1]; Suk Ha Kang[1]; Dong Hyuk Shin[2]; [1]Kookmin University; [2]Hanyang University

The Cross-ARB (C-ARB) process -changing rolling direction by 90 degrees for each ARB cycle- has been carried out up to nine cycles on a commercially pure 1050 Al alloy to obtain ultra-fine grained microstructure. The C-ARB process was adapted with an expectation of increasing ductility of the severely deformed alloy. Microstructures of the C-ARB processed aluminum alloy were examined as a function of accumulated total strain and direction of the rolling. Mechanical properties including hardness and tensile property of the processed Al alloy were also investigated. Grain sizes of the C-ARB processed alloy were found to vary across thickness of the processed alloy plate. Tensile strength of the processed 1050 Al alloy increased from 100MPa to 160MPa. Tensile elongation varied depending on number of process cycle, tensile axis, and rolling direction, but up to 15% of failure strain was measured from a specimen that experienced six C-ARB cycles.

2:40 PM Invited

High Angle Boundary Formation in Dynamically Recoverved Materials during Severe Hot Forging: *Taku Sakai*[1]; [1]University of Electro-Communications

The evolution mechanisms of new high-angle boundary as well as ultra-fine grains in large strain were studied using dynamically recovered materials, such as ferritic steels, aluminum and magnesium alloys, by means of multidirectional forging (MDF). The compression tests were carried out using rectangular samples with consequent changing of loading direction in 90º through three of mutually perpendicular axes. The structural changes can be characterized by the evolution of deformation bands, such as kink and microshear bands at moderate strains. MDF accelerates the evolution of many mutually crossing kink and microshear bands developed in various directions. The (sub)grains become more equiaxed and the misorientations between them gradually increase with increase in cumulative strain, finally leading to the development of new fine-grained structure. It is concluded that the dynamic grain formation can result from a kind of continuous reactions taking place during deformation, i.e. continuous dynamic recrystallization.

3:00 PM

Principles of Grain Refinement in Processing by ECAP: Cheng Xu[1]; Minoru Furukawa[2]; Zenji Horita[3]; *Terence G. Langdon*[1]; [1]University of Southern California; [2]Fukuoka University of Education; [3]Kyushu University

Equal-channel angular pressing (ECAP) may be used to achieve very significant grain refinement in bulk materials. Typically, the materials processed by ECAP have ultrafine grain sizes within the submicrometer range. This paper examines the homogeneity and the microstructural characteristics of pure aluminum and aluminum-based alloys processed by ECAP. Emphasis is placed on the development of a homogeneous ultrafine-grained microstructure with increasing numbers of passes through the ECAP die. The experimental observations are used to develop a representative model that provides a satisfactory explanation for grain refinement in ECAP.

3:15 PM

Bottom Up Fabrication of Bulk Nanocrystalline Materials Using Severe Plastic Deformation (SPD): Consolidation of Nanoparticles via Equal Channel Angular Extrusion (ECAE): *Ibrahim Karaman*[1]; Mohammed Haouaoui[1]; Hans J. Maier[2]; [1]Texas A&M University; [2]University of Paderborn

SPD techniques can be used to refine grains of pure elements down to submicron range, however, achieving grain sizes below 100 nm in bulk (all dimensions in cm range) with considerable ductility is still a challenge. Other available methods of fabricating nanocrystalline materials also suffer from the difficulty of producing bulk samples. In this study, we utilize ECAE as a consolidation technique for controlling grain size from tens of nanometer to micron range by controlling the initial particle size. With this method, we obtained near full density Cu samples with grain sizes below 100 nm, diameters more than 1.5 cm and lengths of 8 cm and longer. The preliminary results showed UTS levels as high as 800 MPa with fracture strains on the order of 5 to 8%. In this presentation, the challenges and opportunities for utilizing ECAE as a powder consolidation technique and our recent findings will be discussed.

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Consolidation of Nanostructured and Ultrafine Grained Metal Powders Using Equal Channel Angular Pressing: *Deliang Zhang*[1]; Peng Cao[1]; Hongbao Yu[1]; Kenong Xia[2]; Xiaolin Wu[2]; Stiliana Raynova[1]; [1]University of Waikato; [2]University of Melbourne

Nanostructured and ultrafine grained metal powders such as Cu, Al and Ti were produced by using high energy mechanical milling. These powders have been consolidated using a typical severe plastic deformation process, equal channel angular pressing (ECAP) to utilise the large amount of shearing in ECAP to enhance the sintering effect. Microstructural characterisation, microhardness testing and tensile testing of the bulk samples are conducted to investigate the effects of ECAP conditions such as temperature, forward pressure and back pressure on the grain sizes and quality of the bulk samples produced. The fracture surfaces of the tensile test samples and the shape change of powder particles that occurs during ECAP are also examined to determine the degree of atomic bonding between powder particles achieved by ECAP and to establish the factors which affect it. This paper is to report and discuss the major findings of this study.

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ECA Pressing up to Failure of Oxygen-Free Copper: Structure, Properties, Effect of the Route: *Sergey Dobatkin*[1]; Jerzy Szpunar[2]; Alexander Zhilyaev[3]; Artem Kuznetsov[1]; [1]A.A.Baikov Institute of Metallurgy and Materials Science; [2]McGill University; [3]Institute of Metals Superplasticity Problems

Structure and mechanical properties of oxygen-free copper depending on the route of ECA pressing at very high strain were studied. Deformation was performed at an angle of 90° between the channels. The maximum number of passes upon deformation by routes A, Bc, and C was N=25. The TEM and EBSD examination revealed the appearance of subgrains and sub-micron grains. The average size of structure elements was 200-300 nm (by TEM) and 250-450 nm (by EBSD). The fraction of high-angle boundaries at N=4 is between 69 and 77%. The equiaxed structure is formed most rapidly upon deformation by route Bc. All strength characteristics have the maximum values after route Bc. Elongation decrease at the early stage of ECA pressing, but then it is stabilized or grow. An increase in plasticity is most pronounced upon deformation by route Bc after sufficiently high strain.

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4:10 PM Invited

Plastic Strain-Induced Grain Refinement at the Nanometer Scale in Cu: *Ke Lu*[1]; [1]Institute of Metal Research, Chinese Academy of Sciences

Formation of ultafine grains via severe plastic deformation in various metals has been studied extensively. Nevertheless, strain-induced grain refinement in the nanometer scale has not yet been fully understood. Plastic deformation mechanism and corresponding dislocation activities in nano-sized grains differ significantly from those in coarse grains. A different underlying mechanism for formation of nano-size grains is anticipated. In the present talk, microstructural evolution of pure Cu processed by means of surface mechanical attrition treatment (SMAT) was investigated by means of TEM observations. Grain refinement processes varying from micro- to nano-scale have been examined systematically within the SMAT sample in which a gradient microstructure is achieved with an average grain size of about 10 nm in the top surface layer. Detailed microstructure features together with analysis of the refinement mechanism of nano-sized grains will be presented. Both dislocation activity and mechanical twinning play a key role in the refinement process.

4:30 PM Invited

Scaling Analysis of Boundary Spacing in Nanostructured Metals: *Xiaoxu Huang*[1]; Niels Hansen[1]; [1]Riso National Laboratory

In the last symposium on Ultrafine grained materials (UFG III), we illustrated the importance in the selection of observation planes for pre-

cise characterization of ultrafine grained or nanostructured metals produced by severe plastic deformation. In this study we quantify the boundary spacing on appropriately selected sample planes as a function of plastic strain. Pure Ni samples deformed by HPT to strains above 10 and commercial purity Al samples deformed by cold rolling to strains above 5 are observed in transmission electron microscopy. The distribution of boundary spacing at different strains is measured and analysed to understand the scaling behaviour during the plastic deformation. The results are discussed in terms of the principles that govern the structural evolution during the deformation.

4:50 PM Invited

Experimental Study and Computer Modeling of High Pressure Torsion: *Igor V. Aleksandrov*[1]; Gyorgy Krallics[2]; Jan Bonarski[3]; Marina Zhilina[1]; Anna Dubravina[1]; Irina Shaimardanova[1]; [1]Ufa State Aviation Technical University; [2]Budapest University of Technology and Economics; [3]Polish Academy of Sciences

High pressure torsion (HPT) is one of most wide-spread schemes for severe plastic deformation. This scheme is often applied for analysis of scientific aspects, connected with formation of bulk ultrafine-grained (UFG) and nanostructured states. At the same time the investigation of the HPT process is a topical issue. This is connected with its multiple-factor character.In this work we present the results of experimental investigations and computer simulation of processes, accompanying HPT of pure copper. Analysis of the material flow features was made in frames of the developed analytical model and the finite element method. The process of the preferred orientations' formation was studied in frames of the viscous-plastic self-consistent model. The interrelation between the components of the stress-strain state and the features of structure- and texture-formation in bulk billets, subjected to HPT, was revealed.

5:10 PM Invited

FEM Analysis of Different Aluminum Alloys Severely Strained by Multipass ECAP: Material Properties and Geometry Effects on Deformation Behavior: *Emanuela Cerri*[1]; Paola Leo[1]; Pier Paolo De Marco[1]; [1]University of Lecce

Three-D FEM simulations of both one and four ECAP passes of different aluminium alloys were performed in order to investigate the deformation state of processed workpiece and, moreover, the effect of different Strain Hardening Rate (SHR) and die geometry (in term of variation of outer angle die) on deformation behaviour. FEM analysis showed a lower equivalent plastic strain on outer side of both cross and longitudinal sections of billets after one and four passes. These results were confirmed both by HV hardness and microhardness test on the same sections of ECAP processed specimens and by microstructural investigations. Moreover FEM analysis indicated that as alloys SHR increases a greater strain inhomogeneity is obtained on cross section of processed specimen. The same effect was observed as the outer angle die increases.

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Influence of Die Features on the ECAP Process: *Ralph J. Hellmig*[1]; [1]Clausthal University of Technology

It has been demonstrated earlier that using a dislocation density based constitutive model is suitable for determining the evolution of microstructure, mechanical properties and texture due to ECAP processing [1,2]. Using FEM simulation, it is also possible to investigate the homogeneity of deformation due to various processing conditions. In this work, the influence of typical ECAP die features (channel geometries; cross-section reduction; various pressure conditions inside the channel, for example due to homogeneous and inhomogeneous backpressure) is investigated using FEM simulation based on the mentioned constitutive model. The aim of this study is to evaluate the advantages/disadvantages of typical ECAP die designs and processing conditions. [1]Baik SC, Hellmig RJ, Estrin Y, Kim HS: Z. Metallkd. 94 (2003) 754-760. [2]Baik SC, Estrin Y, Hellmig RJ, Jeong HT, Brokmeier HG, Kim HS: Z. Metallkd. 94 (2003) 1189-1198.

Wechsler Symposium on Radiation Effects, Deformation and Phase Transformations in Metals and Ceramics: Irradiation Microstructure/ Microchemistry

Sponsored by: The Minerals, Metals and Materials Society, ASM International, TMS Structural Materials Division, ASM Materials Science Critical Technology Sector, TMS Materials Processing and Manufacturing Division, TMS/ASM: Mechanical Behavior of Materials Committee, TMS/ASM: Nuclear Materials Committee, TMS/ASM: Phase Transformations Committee

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Monday PM — Room: 208
March 13, 2006 — Location: Henry B. Gonzalez Convention Ctr.

Session Chairs: Steven J. Zinkle, Oak Ridge National Laboratory; Roger E. Stoller, Oak Ridge National Laboratory

2:00 PM Invited

Effects of Irradiation on Stress Corrosion Cracking of Austenitic and Ferritic-Martensitic Steels in Supercritical Water: *Gary S. Was*[1]; Sebastien Teysseyre[1]; Jiao Zhijie[1]; Gaurav Gupta[1]; [1]University of Michigan

This paper presents the effect of irradiation on the stress corrosion cracking behavior of irradiated austenitic and ferritic-martensitic (F-M) alloys in supercritical water, in support of the supercritical water reactor concept. Austenitic alloys 304L, 316L, 690 and 800H and F-M alloys T91, HCM12A and HT-9 were irradiated with 2-3 MeV protons to doses between 3 and 10 dpa over the temperature range 400-500°C and tested in constant extension rate mode in deaerated supercritical water at temperatures of 400 and 500°C. Results showed that the austenitic alloys exhibited a substantial increase in IG cracking over the unirradiated condition. Of the F-M alloys, only HT-9 exhibited IG cracking in the irradiated condition. The dependence of IASCC on dose, temperature and the correlation with microstructure will be presented in an effort to identify the microstructure changes responsible for enhanced IGSCC in supercritical water.

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Thermal and Radiation-Induced Segregation in Model Ni-Base Alloys: *Todd R. Allen*[1]; Lizhen Tan[1]; Gary S. Was[2]; [1]University of Wisconsin; [2]University of Michigan

Generation IV nuclear energy systems will operate at higher temperatures than current light water reactors and Ni-base alloys are receiving attention as core materials. One aspect of the radiation response of Ni-base alloys to radiation that is not well understood is grain boundary segregation. In this work, three alloys, specifically Ni-18Cr, Ni-18Cr-9Fe, and Ni-18Cr-0.08P were given a series of thermal treatments and quenching to understand the development of thermal non-equilibrium segregation. Additionally, they were irradiated using 3.2 MeV protons at temperatures from 200-500°C to doses up to 1 dpa. Grain boundary segregation was measured with Auger Electron Spectroscopy and Scanning Transmission Electron Microscopy with Energy Dispersive Spectroscopy. Under irradiation, the addition of iron to Ni-18Cr reduced the grain boundary chromium depletion, while the addition of phosphorous to Ni-18Cr increased the grain boundary chromium depletion. Chromium enriches in Ni-18Cr and Ni-18Cr-0.08P due to thermal treatment, but depletes in the Ni-18Cr-9Fe.

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Radiation Stability of Oversize Solute Additions in Austenitic Stainless Steels: *Micah J. Hackett*[1]; Gary S. Was[1]; Jeremy T. Busby[2]; [1]University of Michigan; [2]Oak Ridge National Laboratory

The addition of oversize solutes, such as hafnium or zirconium, to austenitic stainless steel may delay or reduce radiation damage through the trapping and enhanced recombination of point defects. Previous work has

shown reductions in void swelling and radiation-induced segregation in addition to a change in the dislocation microstructure. Varying levels of Zr have been added to Fe-14Cr-14Ni and Hf to Fe-17Cr-14Ni and irradiated with 3.2 MeV protons up to doses of 10 dpa at temperatures of 400°C. Void swelling was measured from the void size distribution using transmission electron microscopy. Dark field TEM imaging was used to determine the dislocation size and density, and RIS was measured using STEM-EDS. Improvements in microstructure and microchemistry of the irradiated oversize solute alloys are demonstrated relative to reference 316SS. Void swelling is delayed until higher doses and radiation hardening is reduced for the Hf alloys. A reduction in RIS is also observed.

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Role of Grain Boundary Engineering in Mitigating IASCC in F-M Alloy HT-9: *Gaurav Gupta*[1]; Gary S. Was[1]; [1]University of Michigan

Ferritic-martensitic alloys have been identified as candidate core structural alloys for the supercritical water reactor (SCWR). Studies have shown that F-M alloys experience high oxidation rate in SCW. They exhibit low susceptibility to SCC, except HT-9 which has shown evidence of cracking in SCW at 400-500°C. HT-9 was irradiated at 400 and 500°C using 2 MeV protons to a dose of 7 dpa and tested in constant extension rate mode at 400 and 500°C in deaerated SCW. Proton irradiation enhanced cracking susceptibility in 400°C SCW with the lower irradiation temperature exhibiting more cracks and a higher maximum crack depth. Grain boundary engineering (GBE) is being explored as a means of reducing the susceptibility of HT-9 to SCC/IASCC in SCW. GBE has already proved beneficial in improving creep properties of T91. Results of CERT tests conducted on unirradiated/irradiated HT-9 in argon and SCW will be presented.

3:25 PM Break

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The Change in the Hardness of LCAC, TZM, and ODS Molybdenum in the Post-Irradiated and Annealed Conditions: *Brian Vern Cockeram*[1]; Richard W. Smith[1]; Lance L. Snead[2]; [1]Bechtel-Bettis; [2]Oak Ridge National Laboratory

An indirect measure of defects and recovery can be obtained using hardness measurements. Hardness measurements were performed on wrought Low Carbon Arc Cast, TZM, and ODS molybdenum in the post-irradiated and annealed condition to determine the kinetics for defect mobility. Irradiations performed in HFIR at 270C to 600C were shown to result in relatively large increases in hardness (54-100%), while small increases in hardness (-11% to 18%) were observed for irradiations at 870-1100C. The kinetics for hardness recovery for irradiations at 270-605C were determined by performing isochronous anneals. Recovery is observed to begin at about 600C and was completed at 1100C for both LCAC and ODS. The activation energy for recovery was determined to be about 4 eV for LCAC and ODS, which is comparable to values reported in literature for molybdenum self-diffusion. TZM exhibits much slower recovery kinetics, which can be explained by the presence of carbon in solution.

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Effect of Self-Irradiation on Bulk Swelling of Plutonium Alloys: *Christophe Thiebaut*[1]; Nathalie Baclet[1]; Pierre Giraud[1]; Pascale Julia[1]; Brice Ravat[1]; [1]CEA Centre De Valduc

Several studies show that plutonium alloys present bulk swelling. More precisely, length (as measured by dilatometry) and cell parameter (as measured by X-ray diffraction) increase with time and reach a saturation after a few months. This is very comparable to the phenomenon observed on both ceramics and metallic alloys exposed to radiation. This bulk swelling can be correlated to self-induced radiation due to the decay of the different plutonium isotopes (238Pu, 239Pu, 241Pu and 242Pu) which also induce helium that tends to forms clusters, then bubbles. Many experimental and theoretical results have already been published. The goal of this paper is to review some of the results and to propose a strategy for both experiments and modelling to try to answer some of the remaining questions regarding swelling and more generally self-irradiation defects in plutonium alloys.

NOTES