MONDAY AM

AIME/TMS KEYNOTE ADDRESS
"FutureView...A Look Ahead"
Daniel Burrus
11:30am-1:00pm
Convention Center, Presidential Ballroom

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Tutorial Luncheon Lecture
"Advanced Rechargeable Batteries: A Materials Science Perspective"
Donald R. Sadoway
12:00noon-1:30pm
Convention Center, Lincoln C

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AIME & TMS Banquet & Awards Presentation
6:00pm Reception
7:00pm Dinner
Convention Center, Presidential Ballroom

+Indicates Student

Advanced Technologies for Superalloy Affordability: Development of New Technology

Sponsored by: Structural Materials Division, High Temperature Alloys Committee
Program Organizers: K. M. Chang, West Virginia University, Mechanical & Aerospace Engineering, Morgantown, WV 26506 USA; K. R. Bain, GE Aircraft Engines, Cincinnati, OH 45215 USA; D. Furrer, Ladish Company, Cudahy, WI 53110 USA; S. K. Srivastava, Haynes International, Kokomo, IN 46904 USA

Monday AM — Room: Canal C
March 13, 2000 — Location: Opryland Convention Center

Session Chairs: Keh-Minn Chang, West Virginia University, Morgantown, WV 26506 USA; John J. deBarbadillo, Special Metals Corporation, Huntington, WV 25705 USA

8:30 AM Keynote
Initiatives for Superalloy Affordability: *Malcolm C. Thomas*[1]; Robert E. Schafrik[2]; James C. Williams[3]; [1]Rolls-Royce Allison, P.O. Box 420, Indianapolis, IN 46206-0420 USA; [2]GE Aircraft Engines, One Neumann Way, MD H85, Cincinnati, OH 45215 USA; [3]The Ohio State University, 477 Watts Hall, 2041 College Rd., Columbus, OH 43210 USA

Modern superalloy forgings and castings have enabled significant increases in turbine engine performance, which have historically been driven primarily by military requirements. The current situation is significantly different, with reduced military budgets for propulsion, and increasing demands from both civil and military customers for affordable solutions to performance requirements. One result of this shift in emphasis has been the initiation of several programs to reduce the cost of these increasingly complex materials. This paper will review some of the work currently being undertaken both at engine manufacturers, and at component suppliers in consortia such as the Engine Supplier Base Initiatives and the Metals Affordability Initiative. The creation of such consortia to reduce component cost has made significant progress possible in focusing the entire supply chain and the customer on this critical issue of affordability

8:55 AM Invited
Application of Lean Concepts to the Aerospace Forging Value Stream: *Dan Krueger*[1]; Rod Boyer[2]; David Furrer[3]; Mary Lee Gambone[4]; Beth Lewis[5]; [1]GE Aircraft Engines, One Neumann Way, MD H85, Cincinnati, OH 45215 USA; [2]Boeing Company, Commercial Airplanes Grp., Seattle, WA 98124 USA; [3]Ladish Company, Inc., 5481 S. Packard Ave., Cudahy, WI 53110 USA; [4]Rolls-Royce Allison, P.O. Box 420, Indianapolis, IN 46206-0420 USA; [5]Wyman Gordon Company, 244 Worcester St., Grafton, MA 01563 USA

Forged components comprise approximately one-third the cost of a propulsion system, and are major cost drivers for airframe systems. Traditionally, cost reduction efforts have focused on improving individual operations or steps in the value stream. A new U.S. Air Force ManTech program, Forging Supplier Initiative, has been initiated to achieve a significant reduction in cost and cycle time through improvements across the entire Supplier-OEM value stream for forged airframe and gas turbine engine components, from raw material order to the finished, ready to install component. Lean Manufacturing, which encompasses a total waste reduction strategy based on a thorough understanding of value for all manufacturing operations in the supply chain, along with forging, machining and modeling technology improvements, must be exploited to achieve the cost and cycle time reduction goals. This paper describes the Phase I approach and progress in the Forging Supplier Initiative program being performed by the General Electric-Lean Industrial Forging Team (LIFT) Consortium. The objective of Phase I, Analysis and Definition of Cost Reduction Opportunities, is to identify cost and cycle time drivers across the entire forged product value stream for representative airframe and propulsion system forgings, and demonstrate the feasibility and payoff of projects selected to address the major drivers.

9:20 AM Invited
Cost Modeling of Forged Turbine Engine Disks: *Kong Ma*[1]; Kenneth A. Green[1]; [1]Rolls-Royce Allison, P.O. Box 420, Indianapolis, IN 46206-0420 USA

As a part of the NASA funded IDPAT (Integrated Design/Processing Analysis Technology) consortium development program, Rolls-Royce Allison was responsible to develop a cost model for forging and machining of turbine engine disks. The objective of this task was to develop a geometric feature based software design tool, which can assist preliminary design to perform trade-off studies in a qualitative fashion. The system consists of generic cost related design/manufacturing rules and allows users to define their company/process specific variables associated with these rules. The user can use a graphic user interface to sketch the design section, then the system will report the cost impact based on the design changes from the base line.

9:45 AM Invited
ATS Advanced Turbine Airfoil Manufacturing Technology Program: *Mei Ling Carolyn Henne*[1]; John Brinegar[1]; Albert Hines[1]; [1]Howmet Research Corporation, 1500 S. Warner St., Whitehall, MI 49461 USA

The purpose of the Advanced Turbine Airfoil Manufacturing Technology Program is to develop single crystal and directionally solidified casting technologies to benefit Advanced Turbine Systems (ATS) industrial and utility gas turbine engines. Traditionally, single crystal investment casting technologies have been utilized for aircraft gas turbine blades where yields of 95% and higher are commonly achieved. These yields are the result of understanding the relationship between alloy, geometry and process conditions. These relationships have been developed iteratively over the past 30 years. The application of this knowledge to Industrial Gas Turbine (IGT) sized castings has demonstrated that the technology involved must be optimized to obtain similar quality and yields of the smaller aircraft turbine counterparts. The goal of this program is to develop the technology utilized for IGT components so that casting yields, furnace up time and direct costs are impacted. This presentation will focus on the thermal resistances to heat removal from an IGT part. Addressing these resistances to heat transfer in a casting process provide guidance on where improvements can be made. Efforts have been directed toward understanding these resistances by employing finite-element-modeling (FEM). Modeling has also been utilized to determine the effects of the thermal resistances on typical IGT, single crystal microstructural defects. Additional efforts involve benchmarking the state-of-the-art in IGT production via microstructural and crystal quality evaluations. Freckle and grain-associated defects are also examined in the evaluations.

10:10 AM Break

10:25 AM Invited

Spraycast-X® for Aerospace Applications: *Thomas Tom*[1]; Greg Butzer[2]; Kim Bowen[3]; [1]Howmet Research Corporation, 1500 S. Warner St., Whitehall, MI 49461-1895 USA; [2]Spraycast Technologies International, L.L.C., Whitehall, MI 49461-1895 USA; [3]Cannon-Muskegon Corporation, Muskegon, MI 48441 USA

Howmet Corporation has licensed and modified the Osprey®, or spray forming process to produce high quality nickel-base superalloys for gas turbine engine applications. The modified process, known as the "Spraycast-X®" process, combined vacuum induction melting technology with high purity argon gas atomization to produce ring and case preform products. This process yields a product with a fine grain homogeneous microstructure, improved machinability, ability to process previously non-forgeable alloys, and an economic benefit that indicate savings of up to 30% over its ring rolled counterpart. Additionally, the Spraycast-X® process results in lead-time reductions of up to 75% over ring rolled components. A description of the process, along with data that substantiates these claims, will be presented.

10:50 AM Invited

Enhanced Powder Metallurgy (P/M) Processing of UDIMET® 720 AE1107C (T406) Turbine Disks: *Gary A. Miller*[1]; Kenneth A. Green[2]; Tony Banik[3]; Joseph Lemsky[4]; [1]Concurrent Technologies Corporation, 1450 Scalp Ave., Johnstown, PA 15904 USA; [2]Rolls-Royce Allison, P.O. Box 420, Indianapolis, IN 46206-0420 USA; [3]Special Metals Corporation, 100 Industry Lane, Princeton, KY 42445 USA; [4]Ladish Company Inc., 5481 S. Packard Ave., Cudahy, WI 53110-8902 USA

Enhanced powder metallurgy (P/M) processing of Udimet 720 has been evaluated as an approach for improving the quality, and concurrently, reducing the cost of AE1107C (T406) turbine disks. Enhanced P/M processing combines several technologies: high-yield production of fine powder (-270 mesh); low extrusion ratio (3:1) for converting as-HIPed material to billets; isothermal forging of disk preforms to near-net shape; and selective ultrasonic inspection. Having achieved acceptable mechanical properties, the viability of this combination of technologies depends upon component performance in cyclic spin and spin burst tests and engine tests as well as verification of projected cost savings. Results obtained to date confirm the acceptability of material produced using this combination of technologies. Technology implementation hinges on the component and engine test results and completion of the cost/benefit analysis which remain to be performed. Technology assessment activities including defect migration and flow modeling; residual stress measurement, modeling, and mitigation approaches; HIP modeling; and seeding are discussed.

11:15 AM Invited

The Castability and Mechanical Properties of Nickel Superalloys Cast Using Thermally Controlled Solidification: *Sanjay Shendye*[1]; M. L. Gambone[2]; Paul P. Andrews[3]; Michael Tims[4]; [1]PCC Structurals Inc., 4600 S.E. Haney Dr., Portland, OR 97206 USA; [2]Rolls-Royce Allison, P.O. Box 420, Indianapolis, IN 46206-0420 USA; [3]Rolls-Royce, plc, P.O. Box 31, Derby DE248BJ UK; [4]Concurrent Technologies Corporation, 1450 Scalp Ave., Johnstown, PA 15904 USA

Thermally Controlled Solidification (TCS), a casting process patented by PCC Structurals, has potential to greatly reduce the cost of aerospace structural castings. The response of three nickel superalloys; INCO 718, INCO 939 and RS5; to casting via TCS was studied as part of a program supported by the National Center for Excellence in Metalworking Technology. (RS5 is a superalloy developed a by Rolls-Royce, plc.) The alloys were compared by such characteristics as the ability to fill thin-wall sections, propensity to hot tear, and weld reparability. TCS microstructures were analyzed, and mechanical properties; including tensile, creep, fatigue and damage tolerance; were measured for each of the TCS cast alloys. The castability evaluation plan will be presented in this paper as well as the results and their implication.

Deformation and Stress During Solidification

Sponsored by: Materials Processing and Manufacturing Division, Solidification Committee, Jt. Processing Modeling Analysis & Control Committee, Shaping and Forming Committee

Program Organizers: Brian G. Thomas, University of Illinois, Department of Mechanical and Industrial Engineering, Urbana, IL 61801 USA; Christoph Beckermann, University of Iowa, Department of Mechanical Engineering, Iowa City, IA 52242 USA; Matthew J.M. Krane, Purdue University, School of Materials Engineering, West Lafayette, IN 47907 USA; Srinath Viswanathan, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6083 USA

Monday AM — Room: Johnson A/B
March 13, 2000 — Location: Opryland Convention Center

Session Chairs: Brian G. Thomas, University of Illinois, Mech. & Industrial Eng., Urbana, IL 61801 USA; Christoph Beckermann, University of Iowa, Dept. of Mech. Eng., Iowa City, IA 52242-1527 USA; Matthew J. Krane, Purdue University, School of Matls. Eng., West Lafayette, IN 47907 USA

8:30 AM

An Experimental Study of the Deformation of a Directionally Solidified SCN-ACE Alloy Mush: Ernandes M.S. Rizzo[2]; Venkatesh Raghavendra[1]; Houfa Shen[1]; *Christoph Beckermann*[1]; [1]University of Iowa, Dept. of Mech. Eng., 2412 SC, Iowa City, IA 52242 USA; [2]Centro Federal de Educacao Tecnologica do Espirito Santo, C.P. 5139, Vitoria, ES 29040-333 Brazil

The deformation of a directionally solidified mush of a succinonitrile-acetone (SCN-ACE) alloy is studied experimentally. This alloy not only solidifies dendritically like a metal alloy, but also has mechanical properties that are similar to those of metals near the melting point. A test cell was designed that allows for the directional solidification of the alloy and the controlled compression of the mush that forms. Measurements during the deformation include the local displacement and deformation rate of the solid, the flow patterns in the liquid, temperatures, and liquid concentrations. Results are presented for a

range of initial compositions, cooling rates, and deformation amounts. The measurements are suitable for validation of future models. The experiments are relevant, for example, to the deformation of a partially solidified strand during continuous casting of steel slabs.

8:50 AM

Relation Between Tensile and Shear Strengths of the Mushy Zone in Solidifying Aluminium Alloys: Stephen S. Instone[1]; Taro Sumitomo[1]; *Arne K. Dahle*[1]; [1]The University of Queensland, Dept. of Ming., Mins. and Mats. Eng., Brisbane, Qld 4072 Australia

Strength measurements reported in the literature show a significant deviation in results for semi-solid material tested in shear and in uniaxial tension. This therefore raises the question of whether different deformation mechanisms apply and which are the important with respect to predicting the formation of various defects, such as hot tearing, surface cracking and burst feeding. In this work, the strength development during solidification of various aluminium alloys has been measured with two different techniques-horizontal tensile testing and direct shear cell testing. The strength results from the two methods correspond to a much higher degree than suggested by the results presented in the literature. Constitutive equations for the mechanical properties of the mushy zone over the whole solid fraction regime, ie. from coherency to complete solidification, can be developed based on these strength measurements. These equations can be used for the prediction of stress development as well as defect formation. An important component of the analysis of the mechanical properties of the mushy zone is the fraction of the cross-sectional area that is capable of supporting an applied load through the formation of a continuous solid network. Consequently, the formation of solid-solid bridges and their contribution to the strength of the mushy zone was investigated by comparing mushy zone strength to measurements of tensile strength at temperatures just below the solidus temperature. This information was then used to estimate the fraction of the cross-sectional area of the mushy zone where solid-solid bridging had occurred.

9:10 AM

Tensile Deformation Behaviour at Above Solidus Temperatures in Aluminium Alloy 5083: *John Anthony Spittle*[1]; Jonathan James[1]; Stephen G.R. Brown[1]; Michael E. Keeble[1]; [1]University of Wales, Matls. Eng. Dept., Singleton Park, Swansea, Wales SA28PP UK

A tensile testing technique has been developed specifically for examining true stress/true strain behaviour at above solidus temperatures. ASSET (the Advanced Semi-Solid Elongation Test) applies AC Joule heating to rapidly reheat specimens from DC-cast ingots to the test temperatures. Specimen and grip geometries are designed using a finite difference thermal model, such that a test temperature is maintained at ~+/-2 degrees K over a gauge length of 20mm. Strain measurements are carried out using a non-contact linescan camera method. The fraction liquid at a given test temperature is determined using a thermodynamic model assuming Scheil non-equilibrium freezing. The test has been applied to the study of 5083 aluminium alloy at several test temperatures and crosshead movement rates. The data has been evaluated and plotted as true stress/true strain and the curves have been analysed using a simplex approach. The influences of fraction liquid, strain rate, strain and microstructure on deformation characteristics are described and discussed.

9:30 AM

Mechanical Behavior of Carbon Steels in the Temperature Range of Mushy Zone: *Dong Jin Seol*[1]; *Young Mok Won*[1]; *Tae-jung Yeo*[1]; *Kyu Hwan Oh*[1]; [1]Seoul National University, Matls. Sci. and Eng., San 56-1 Shinrim-dong, Lab. of Matls. Deformation and Processing, Seoul 151-742 Korea

Tensile strength and ductility of carbon steels have been measured in the temperature range of mushy zone by the in-situ melting tensile test technique with Gleeble system. The specimen was melted and cooled to the test temperature before the tensile deformation in order to get the mechanical properties subject to the continuous casting process. During hot tensile test, a ceramic fiber tube was used to reduce the radial temperature gradient in the heated specimen. Tensile strength of carbon steels in the temperature range of mushy zone increased with decreasing test temperature, and was well described by the modified yield criterion for porous metals. The measured zero strength temperature (ZST and zero ductility temperature) (ZDT) were related to the solid fractions evaluated by the numerical simulation of microsegregation. The characteristic solid fractions of ZST and ZDT which corresponded to 0.75 and 0.99, respectively, were well described by the prediction equation on ZST and ZDT at given steel compositions and cooling rates. KEY WORDS: mushy zone; zero strength temperature (ZST zero ductility temperature) (ZDT).

9:50 AM Break

10:20 AM

A New Hot Tearing Criterion: Application to DC Casting of Aluminum Alloys: *Jean-Marie Drezet*[1]; Michel Rappaz[1]; [1]Laboratoire de Metallurgie Physique, Ecole Polytechnique Federale de Lausanne, MX-G, Lausanne CH-1015 Switzerland

Hot tear is one of the most serious defects which a casting can suffer. It represents a major limitation to the production of foundry cast parts and to the productivity of continuous casting processes such as the direct chill casting of aluminum alloys. As an example, the casting speed of the direct chill casting of billets is limited for some aluminium alloys because of their high propensity to develop hot tears which initiate at non zero liquid fraction at the bottom of the sump. In order to predict the occurrence of hot tears in solidifying parts, a hot tearing criterion based on the ability of the interdendritic flow of liquid to compensate for the thermally-induced deformation of the roots of dendrites has been recently derived by Rappaz, Drezet and Gremaud. Based upon a mass balance performed over the liquid and solid phases, this criterion accounts for the deformation of the solid skeleton perpendicularly to the growing columnar dendrites and for feeding of the interdendritic liquid: it allows the calculation of the maximum strain rate that the roots of the dendrites can undergo without initiation and/or propagation of hot tears. The present paper gives a summary of the main features and assumptions of the new hot tearing criterion. The equations defining the hot cracking sensitivity index in the particular case a thermally-induced deformation rate which is uniform in the mushy zone are presented. Then, the model is applied to the particular case of the DC casting of billets of aluminum alloys. The maximum strain rate sustainable by the mushy zone is derived at the bottom of the sump and in the primary cooling zone. It is demonstrated that the bottom of the sump is more sensitive to hot tearing than the primary cooling zone, thus limiting the casting speed and therefore the productivity of the process.

10:40 AM

Application of Solidification-Stress Model to Predict Critical Shell Thickness for Breakouts During Continuous Casting of Steel: Chunsheng Li[1]; *Brian G. Thomas*[1]; [1]University of Illinois, Mech. & Industrial Eng., 140 Mech. Eng. Bldg., 1206 W. Green St., Urbana, IL 61801 USA

During continuous casting, excessive gap formation in the mold can lead to a locally thin solidified shell with a higher surface temperature. This can cause a breakout if the strength of the shell is insufficient to withstand the ferrostatic pressure at mold exit. A finite element model has been developed to simulate thermal and mechanical behavior of the solidifying shell during continuous casting of steel both in and below the mold. It features an elastic-viscoplastic creep constitutive equation that accounts for the different responses of the semi-solid, delta-ferrite, and austenite phases. The model is applied to predict temperature, stress, and strain in a section through the steel shell cast under conditions that lead to varying degrees of shell growth and surface cooling. At mold exit, ferrostatic pressure is applied and the mechanical response is predicted. The results suggest critical conditions that lead to excessive strain and failure of the shell for different steel grades.

11:00 AM

Cracking Phenomena of AISI 304 Stainless Steel Produced by Twin Roll Strip Casting Process: D. K. Choo[1]; *S. I. Jeong*[1]; M. J. Ha[1]; S. H. Kim[1]; S. Lee[2]; [1]Research Institute of Industrial Science & Technology, Strip Casting Project Team, P.O. Box 135, Pohang, Kyongbuk 790-600 Korea; [2]Pohang University of Science & Technology, Matl. Sci. & Eng., San 31 Hyojadong, Pohang, Kyongbuk 790-600 Korea

Cracks occurring on the surface of AISI 304 stainless steel produced by strip casting process was investigated and the causes for their occurrence were postulated. The sections of as-cast strip near the cracked region were cut and polished to reveal microstructural change, and the cracked region was fractured to investigate the location of crack initiated area using optical and scanning electron microscopes. The fractography showed that the crack was initiated at the tip of dendrite of solidified shell and propagated along the path to the segregated liquid film between primary dendrites and the fractured surface was heavily oxidized from atmosphere, as this was typical in solidification cracking at high temperature. The reason for the occurrence of solidification cracking in the strip casting process was uneven stress distribution in the solidified shell during solidification: when the local tensile stress in the delayed solidification region exceeded the critical strain limit of the shell at high temperatures, the crack would be formed at delayed solidified shell. The causes for the uneven solidification were local heat transfer barriers on roll surface, such as contaminated oxide debris on roll surface, oxide scum entrapped at meniscus and melt level fluctuation. The tendency of crack occurrence was also dependent on the chemical composition of molten steel and the cooling rate of the solidified strip.

11:20 AM

Effect of Gap Distance on the Cooling Behavior and Microstructure of Indirect Squeeze Cast and Gravity Die Cast 5083 Wrought Al Alloy: *Jong Hyeon Lee*[1]; Hyoung Seop Kim[1]; Chang Whan Won[1]; Seong Seock Cho[1]; Byong Sun Chun[1]; [1]Chungnam National University, Rapidly Solidified Matls. Rsch. Ctr., 220 KungDong, Taejon 305-764 Korea

An indirect squeeze casting process applied to a wrought Al alloy (Al-4.7Mg-0.7Mn) was investigated experimentally and numerically. A two-dimensional finite element computer code for fully coupled heat transfer and deformation analysis, ABAQUS, was used to simulate the cooling curves obtained from the experiments. Thermal contraction of the material during solidification creates a cavity between the mold and the cooling material. The formation of this cavity is explained using the calculated results. The experimental and predicted results are discussed in conjunction with the relationships between the cooling rate, microstructure, die geometry and applied pressure. The effect of applied pressure on the macrosegregation is also discussed.

11:40 AM

Computer Based Analysis of Thermal Stresses for Continuous Steel Casting Rate Increase: *Alexey N. Lozhko*[1]; *Viktor M. Olshanski*[1]; *Vladimir I. Timoshpolski*[2]; [1]State Metallurgical Academy of Ukraine, Thermal Eng. Dept., 4 Gagarin Prosp., Dniepropetrovsk UA 320635 Ukraine; [2]Byelorussian State Politechnical Academy, 2 Kondrat Krapiva Str., Minsk BA 220117 Belarus, Republic

The maximum increase in continuous steel casting rate is predetermined by economical reasons. Thermal stresses acting as the factors limiting the process, arise as a result of cooling rate inconsistency between different ingot points. Underestimation of this effect brings forth the appearance of inner cracks or residual stresses. By changing the crystallizer profile it is possible to sufficiently diminish thermal stresses effect on casting rate. The experimental research of thermal stresses during solidification is very costly (in Ukraine). That is why adequate computer modeling of the process is becoming vital. The conjugate 3-D thermo-mechanical state model of the bar-crystallizer system was the basis of the multi-fold analysis of the process. The paper presents the crystallizer profiles computed for certain occurances and the results of their experimental implementation.

Dislocations and Microscale Plasticity Modeling: Theory and Modeling of Dislocations

Sponsored by: ASM International: Materials Science Critical Technology Sector, Materials Processing and Manufacturing Division, Structural Materials Division, Jt. Mechanical Behavior of Materials, Jt. Computational Materials Science & Engineering

Program Organizers: Elizabeth Holm, Sandia National Laboratories, Albuquerque, NM 87185-1411 USA; Diana Farkas, Virginia Polytechnic Institute and State University, Department of Materials Science and Engineering, Blacksburg, VA 24061 USA; Jeffrey Rickman, Lehigh University, Department of Materials Science and Engineering, Bethlehem, PA 18105-3195 USA; David J. Srolovitz, University of Michigan, Department of Materials Science and Engineering, Ann Arbor, MI 48109 USA; Vaclav Vitek, University of Pennsylvania, Department of Materials Science and Engineering, Philadelphia, PA 19104 USA

Monday AM — Room: Lincoln A
March 13, 2000 — Location: Opryland Convention Center

Session Chair: Vaclav Vitek, University of Pennsylvania, Materials Science & Engineering, Philadelphia, PA 19104 USA

8:30 AM Invited

Dynamic Simulation of Dislocation Microstructures: *Richard LeSar*[1]; [1]Los Alamos National Laboratory, MST-8, MS G755, P.O. Box 1663, Los Alamos, NM 87545 USA

One approach to bridge the gap between the atomistic scale and macroscopic materials response is a simulation in the intermediate, or mesoscopic, regime that focuses on the collective properties of the defects. For problems in materials deformation, a promising approach is dislocation dynamics, in which the dynamic motion and patterning of the dislocations themselves are simulate. There are a number of challenges in implementing dislocation dynamics, including the accurate treatment of the long-range interactions, the non-linear-elastic short-range interactions, etc. We will briefly review progress to date. We will then present results from a recently-developed three-dimensional method for calculating dislocation microstructures based on Monte Carlo and Kinetic Monte Carlo approaches. The advantages and disadvantages to this approach relative to the more standard dislocation dynamics simulations will be discussed. Time permitting, we will present an alternative approach to simulating dislocation microstructures that yields coarse-grained structures and properties.

9:10 AM

Three-Dimensional Dislocation Dynamics Simulations of Stacking Fault Tetrahedra Formation using Anisotropic Elasticity: *Moono Rhee*[1]; Brian D. Wirth[1]; James S. Stölken[1]; [1]Lawrence Livermore National Laboratory, Chem. and Matls. Sci. Directorate, P.O. Box 808, L-356, 7000 E. Ave., Livermore, CA 94551 USA

The formation of Stacking Fault Tetrahedra (SFT) in Face-Centered Cubic (FCC) metals is studied using both Molecular Dynamics (MD) based on embedded atom method potentials and Dislocation Dynamics (DD) simulations. MD simulations suggest that SFT form via the spontaneous decomposition of Frank partial dislocation loops into stair-rod partial dislocations and Shockley partial dislocations, which subsequently glide to form the SFT; as initially proposed by Silcox and Hirsch. Three-dimensional DD simulations utilizing fully anisotropic elasticity are performed to study the influence of disloca-

tion mobility, stacking fault energy, and elastic anisotropy on the formation mechanism for a variety of FCC metals. This work is performed under the auspices of U.S. Department of Energy and Lawrence Livermore National Laboratory under contract No. W-7405-Eng-48.

9:30 AM

Simulation of Equilibrium Distribution of Dislocation Structures in Bcc Single Crystals under Cyclic Loading: *S. B. Biner*[1]; J. R. Morris[1]; [1]Ames Laboratory, Iowa State University, Metallu. and Ceramics, Ames, IA 50011 USA

Collective motion of large number of discrete edge dislocations in bcc single crystals under cyclic loading is investigated using a numerical method that combines the finite element method and multi pole expansion algorithm. The dislocations are modeled as line defects in a linear elastic medium. At each instant, superposition is used to represent the solution in terms of the infinite-medium solution for the discrete dislocations and a complementary solution that enforces the boundary conditions. Annihilation of dislocations, generation of new ones and dislocation pinning at obstacles are simulated through a set of constitutive models. The evolution of Bauschinger-effect and hardening and softening behavior is correlated with the cyclic load levels and the parameters of the constitutive model for the collective behavior of dislocations. The details of the implementation of the numerical method for parallel computing in a cluster environment will also be elucidated. This work was performed for the United States Department of Energy by Iowa State University under contract W-7405-Eng-82.

9:50 AM

Kinetics of Slip and Plasticity Including a Distribution of Obstacle Sizes and Load Shedding: *Glenn S. Daehn*[1]; [1]The Ohio State University, Dept. of Matls. Sci. and Eng., 2041 College Rd., Columbus, OH 43210 USA

Over the past few decades there has been much interest in describing plastic deformation as a classical kinetic problem of the thermal activation of a dislocation over a barrier, where an external stress provides a driving force tending to push the dislocation over an obstacle. The approach almost invariably implicitly assumes that the obstacles are of a single uniform size and shape and the driving force at each obstacle is also fixed. These are both clear oversimplifications. Presently the effects of a spectrum of obstacle sizes as well as slip-induced load shedding will be studied and are shown to produce significant changes in the modeled material behavior. A stochastic cellular automaton model is used to construct the model. One of the most exciting aspects of this approach is that using only very simple and reasonable assumptions many commonly-observed creep and plasticity phenomena (such as anelastic backflow and power-law strain-time creep transients) naturally emerge and aspects of this behavior can be correlated to the assumptions in a given model.

10:10 AM Break

10:30 AM

Study of the Dislocation Cores in Bcc Transition Metals Using Bond-Order Potentials: Importance of Directional Bonding: M. Mrovec[1]; R. Porizek[1]; D. Nguyen-Manh[2]; D. G. Pettifor[2]; M. Sob[3]; *V. Vitek*[1]; [1]University of Pennsylvania, Dept. of Matls. Sci. and Eng., 3231 Walnut St., Philadelphia, PA 19104 USA; [2]University of Oxford, Dept. of Matls., Parks Rd., Oxford OX13PH UK; [3]Institute of Physics of Materials, Academy of Sciences, Zizkova 22, Brno, Czech Republic

The core structure of screw dislocations in the 4d (Nb and Ta) and 5d (Mo and W) transition metals is studied by computer simulation using the recently constructed bond-order potentials based on the real-space parametrized tight-binding method. In this framework the energy consists of the bond part that comprises contributions of d electrons, the central-force many-body part that reflects the environmental dependence of overlap repulsion arising from the valence sp electrons and a repulsive pair-wise contribution; the calculations scale linearly with the system size. The potentials have been tested for the accuracy and transferability by evaluating the energy differences of alternate structures and investigating several transformation paths and comparing these calculations with the ab initio results. The study begins with calculations of the gama-surfaces and is followed by simulations of the structures of screw dislocations. The results are compared with analogous studies made using the central-force many-body potentials of the Finnis-Sinclair type. This comparison enables us to assess the importance of directional bonding on the dislocation core structure and thus mechanical behavior of the 4d and 5d transition metals. This research was supported in part by the Advanced Strategic Computing Initiative of the U.S. Department of Energy through LLNL, grant no. B331542 (MM and VV).

10:50 AM

The Barrier Strength of Mismatch Dislocations: *Satish I. Rao*[1]; Peter M. Hazzledine[1]; [1]UES Inc., 4401 Dayton-Xenia Rd., Dayton, OH 45432 USA

In order for layered materials to yield, mobile dislocations must be able to cross the layer interfaces. The barrier to motion through the interface contains several components. In semicoherent multilayers one of the most significant components is the set of mismatch (van der Merwe) dislocations. The separation of these dislocations, d, depends on the lattice parameter mismatch and the degree of coherency, hence on the layer thickness. The barrier stress has two closely related parts, first the requirement to bow the mobile dislocation between the mismatch dislocations and second, the requirement to leave a 'difference' dislocation at the interface. The paper describes EAM atomistic simulations designed to test and refine the analytical estimate for this stress of a Gb/d.

11:10 AM

Systematic Analysis of Dislocation Junction Reactions in Bcc Metals Using Anisotropic Elasticity: *James S. Stölken*[1]; [1]Lawrence Livermore National Laboratory, Chem. and Matls. Sci. Directorate, P.O. Box 808, L-356, 7000 E. Ave., Livermore, CA 94551 USA

Anisotropic elasticity calculations were performed to estimate the intrinsic strength of dislocation junction reactions in both Group VB-VIB transition metals, and Iron. A dislocation phase space description is used to systematically categorize junction formation reactions for dislocations on {110}, {112}, and {123} slip planes: identifying <24 unique junction reactions that comprise the 1176 possible reactions. Regions in which repulsive or neutral dislocation reactions (i.e. jogs) may occur are also identified. The calculations form a critical link between microscale phenomena of dislocation interaction and the formulation of mesoscopic models of crystal plasticity by establishing a taxonomy of dislocation interactions. The resulting catalog of dislocation reactions indicates the relative strength of dislocation junctions, imposes certain symmetry restrictions for physics based hardening models, and suggests specific latent hardening experiments to measure the influence of junction formation on the work hardening of BCC metals. This work is performed under the auspices of U.S. Department of Energy and Lawrence Livermore National Laboratory under contract No. W-7405-Eng-48.

11:30 AM

Primitive Dislocation Loops in Face-Centered Cubic Crystals: *Craig S. Hartley*[1]; [1]U.S. Department of Energy, Office of Science, SC-131, Germantown, MD 20874 USA

The effect of crystal structure on atomic displacements near the dislocation core cannot be included in local continuum models of dislocations. Atomic models of dislocations using appropriate interatomic potentials can provide this information, subject to limitations imposed by the choice of interatomic potential and boundary conditions on the atomic array surrounding the dislocation line. An intermediate approach, the simulation of dislocations by non-local force arrays, shows promise as a method for modeling the atomic arrangements near dislocations and other crystal defects. This method relies on the definition of a "primitive dislocation loop", a non-local continuum analogue to the infinitesimal dislocation loop of local continuum theory. The primitive loop consists of an array of forces applied to the nearest neighbors of an atom. Magnitudes and directions of the forces are chosen so that the far-field displacement field of the array is identical to that of an infinitesimal dislocation loop centered on the atom. The locations of the forces are determined by the crystal structure of the medium, i.e. by the coordination group surrounding an atom. Dislocation lines can then be constructed by superposition of these primitive loops to form various shapes. Since the singular character of the force array is concentrated in the points of application of the forces, whose displacements can be estimated from atomic force constants, there is no singularity in stress or strain at the core of the

dislocation. This model has been employed to determine the displacement fields and energies of dislocations, kinks and jogs in the case of an elastically isotropic, simple cubic lattice, but extension to real structures relies on the construction of appropriate primitive loops. Such loops have been constructed for the body-centered cubic lattice in anisotropic crystals. The present work extends this construction to the face-centered cubic lattice and describes the technique for determining properties of finite dislocation configurations.

11:50 AM

Self-Consistent Modeling of Polycrystal Plasticity: B. Clausen[1]; *Carlos N. Tome*[1]; F. Jean-Prost[1]; M. A.M. Bourke[1]; [1]Los Alamos National Laboratory, MST-8, MS G755, Los Alamos, NM 87545 USA

The utilization of self-consistent modeling (SCM) of polycrystalline plasticity to predict internal and residual stresses in structural materials has increased significantly in the last decade. The constitutive equations for elastic-plastic and visco-plastic self-consistent schemes will be presented and the advantages and limitations of the models will be discussed. At Los Alamos National Laboratory the SCM of several materials has been correlated with in situ neutron diffraction measurements of internal and residual elastic lattice strains. Furthermore, the SCM scheme has been incorporated into finite element codes enabling predictions of complex non-uniform loading and arbitrary geometries. We also discuss the use of SCM as a tool for interrogating the microstructural mechanisms, such as type and characteristics of slip and twinning systems, and their interactions.

General Abstracts: Aluminum and Texture

Sponsored by: TMS

Program Organizers: Mark E. Schlesinger, University of Missouri, Department of Metallurgical Engineering, Rolla, MO 65409-0001 USA; Alton T. Tabereaux, Reynolds Metals Company, Smelter Technology Laboratory, Muscle Shoals, AL 35661-1258 USA; Dan J. Thoma, Los Alamos National Laboratory, Materials Science and Technology, Los Alamos, NM 87545-0001 USA; Patrice E.A. Turchi, Lawrence Livermore National Laboratory, Materials Science and Technology Division, Livermore, CA 94551 USA

Monday AM — Room: Knoxville A
March 13, 2000 — Location: Opryland Convention Center

Session Chair: Mike O'Brien, Lawrence Livermore National Laboratory, Livermore, CA 94551 USA

8:30 AM

Comparison of Microstructure and Texture of AA3XXX Direct Chill Cast Ingot and Strip Cast Slab: J. T. Liu[1]; Y. Liu[1]; *J. G. Morris*[1]; [1]University of Kentucky, Light Metals Resrch. Labs., Dept. of Chem. and Mats. Eng., 177 Anderson Hall, Lexington, KY 40506 USA

Direct chill (DC) ingot and strip cast (SC) slab present significantly different features in microstructure and texture. Both the microstructure and texture of AA3105 DC ingot and AA3015 SC slab were observed in this work for the purpose of determining the difference in microstructure and texture between DC ingot and SC slab. The results show that both the DC ingot and SC slab present a random texture and nearly the same grain structure, however, the dispersion of particles and the solute supersaturation condition of the alloying elements for DC ingot and SC slab are very different. Consequently, the dispersion of particles and the solute supersaturation condition of the alloying elements significantly contribute to the great difference in microstructure and texture evolution between DC ingot and SC slab in the following thermomechanical processing of these materials.

8:50 AM

Earing Behavior of AA6010 Aluminum Alloy with Different Preferred Orientations: Yansheng Liu[1]; Jiantao Liu[1]; Xiang-Ming Cheng[1]; *James G. Morris*[1]; [1]University of Kentucky, Light Metals. Resrch. Labs., Dept. of Chem. and Mats. Eng., 117 Anderson Hall, Lexington, KY 40506 USA

Texture inhomogeneity through the thickness has been found in AA6010 aluminum alloy hot band. Annealing does not remove the inhomogeneity but produces different textures. In order to understand the earing behavior of the materials, samples for earing test were prepared by slicing the original hot band in planes parallel to the rolling plane. Samples with the typical texture at the midplane of the hot band and with the textures at the surface of the hot band were obtained separately. Earing of both the as received samples and annealed samples were measured. The results show that earing of different samples and annealed samples were measured. The results show that earing of different samples are typically controlled by their textures. However, earing of the original hot band can not be simply designated as the average of the several sliced samples.

9:10 AM

Anisotropy and Texture Evolution of Cold-Rolled Al-Mg Alloys: *Seiichi Hirano*[1]; Masaru Nomura[1]; [1]Sumitomo Light Metal Ind., Limited, Rsch. and Dev. Ctr., 1-12 3-chome, Chitose Minato-ku, Nagoya, Aichi 455-8670 Japan

Texture evolution which leads to the earing behavior of a drawn cup of cold-rolled Al-Mg alloy sheet was investigated by two different process materials, with and without intermediate annealing during cold rolling. The samples without intermediate annealing had 6 or 8 ears on the cups, while ones with intermediate annealing had 4 ears. Ears at 0° and 180° to the sheet rolling (RD) are related to the intensity of the Cube and RD rotated Cube texture. 45° ears were related to beta fiber components of the rolling texture, and the ratio of Brass and Cu component intensities along the beta fiber was different between with and without intermediate annealing samples. Texture and microstructure changes associated to the intermediate annealing conditions are also discussed.

9:30 AM

Analysis of Tensile/Compressive Deformation in Zirconium Bent Beams: *G. C. Kaschner*[1]; T. A. Mason[1]; J. F. Bingert[1]; P. J. Maudlin[1]; [1]Los Alamos National Laboratory, Los Alamos, NM 87545 USA

Previous work has demonstrated that the deformation mechanisms of this highly anisotropic low-symmetry metal may be dominated by either slip or twinning depending on strain rate, temperature, and orientation. In the current study, we have loaded basal fiber textured zirconium beams of two orientations in 4-point bending to produce a continuous stress-strain gradient across the thickness of the sample. The macroscopic shape of the cross-sections was used to validate predictive modeling efforts. The predictive modeling is based on an anisotropic yield criterion that is a function of texture and deformation mechanism, ie., slip or twinning. Automated EBSP methods were used to analyze twinning deformation modes as a function of position, and hence sign and magnitude of strain, in the beam. These measurements corroborated the basis for constructing our yield function. Research supported by the US DOE, Basic Energy Sciences, Division of Materials Sciences.

9:50 AM

The Cooling and Solidification Behaviour of Aluminum and Aluminum Alloys Weld: *Kimioku Asai*[1]; Eisaku Tokuchi[1]; [1]Musashi Institute of Technology, Tokyo, Japan

Experiments on weld solidification were successfully carried out in TIG arc spot welding of thin plate. This second research was conducted to establish a practical, convenient method for evaluating the hot cracking susceptibility in Al-alloys weld. In addition to the temperature measurement in welding thermal cycle, the behaviour of the liquid film solidifying in the grain boundary was investigated by revealing dynamically the liquid films in breaking surfaces with a newly developed high-speed breaking machine, and by observing them prudently with SEM. All those results including on solidification rate, cooling rate, temperature gradient, and fraction solid were quantitatively gath-

ered in a diagram named CCSP (Continuous Cooling Solidification Process) diagram. The result of the Varestraint Test carried out to make hot cracking occur was also considered with the same diagram. This series of operation enabled us to discuss the cooling and solidification behaviour of weld in relation to the hot cracking susceptibility.

10:10 AM Break

10:30 AM

Fatigue Crack Initiation in Aluminum Alloys: *Peter S. Pao*[1]; Steven J. Gill[1]; Jerry C. Feng[1]; [1]Naval Research Laboratory, Washington, DC 20375 USA

Fatigue crack initiation from pre-existing corrosion pits of 7075 and 7050 alloys was investigated using blunt-notched WOL specimens. The presence of corrosion pits not only reduces the fatigue crack initiation lives but also lowers the fatigue crack initiation thresholds by half. The effect of aging was studied by comparing the fatigue crack initiation of peakaged 7075-T651 to that of overaged 7075-T7351. At high stresses, 7075-T651 exhibits longer fatigue initiation lives than does 7075-T7351. However, at lower stresses, the difference between the fatigue crack initiation diminishes. The effect of orientation was investigated by comparing the fatigue crack initiation of SL 7075-T651 to that of ST 7075-T651. At high stresses, SL 7075-T651 demonstrates longer fatigue initiation lives than does ST 7075-T651. Again at lower stresses, such differences disappear. Fatigue crack initiation and identification of initiation sites and mechanisms are discussed.

10:50 AM

Improvements of 6063 Al-Alloy for Rapid Extrusions and Possibility of Reducing Their Tails: *Abdel Haleem Ghaneya*[1]; [1]Assiut University, Mining and Metallu. Dept., Egypt

This study was applied on an industrial scale of EgyptAlum Company It is principally divided into two main branches. The first is concerned with the transformation of beta phase into alpha phase, and at the same time, the dissolution of Magnesium silicide precipitate. Both processes lead to ease the fabricability of the alloy by extrusion, even at a rapid rate. The second branch deals with the possibility of reducing ingot tails. Manufacturers require ingots of 6063 free of non-metallic inclusions of both ends. Our trial was carried out to achieve minimum non-metallic inclusions number and size, as well as their distribution per unit area at both ends of ingot. According to the first branch, the temperature of homogenization was found to be 580°C for holding time of 12 hours. This is sufficient for obtaining the alpha phase and for the dissolution of Magnesium silcide precipitate. Cooling was performed by using three fans, each providing 60000 meter cube of air per hour. By this specific cycle (heating, holding, cooling), the beta phase transformation and magnesium silicide precipitation and its coalescence are prevented. As for the second branch, our trials give inconsistent results. Nevertheless 20% of the removed part can be saved.

11:10 AM

Characterization of Oriented Structure in Copper Electrocoatings: Yuliya O. Proshenko[1]; Evgenii P. Kalinushkin[1]; *Oleg B. Girin*[2]; [1]State Metallurgical Academy of Ukraine, Dept. of Phys. Metallu., Prospekt Gagarina 4, Dnipropetrovsk 320635 Ukraine; [2]Ukrainian State University of Chemical Engineering, Dept. of Matls. Sci., Prospekt Gagarina 8, Dnipropetrovsk 320005 Ukraine

A comprehensive study into structure evolution in copper electrolyte coatings at the stages of nucleation and growth of the major component of texture was carried out using nonconventional X ray diffraction techniques in combination with scanning electron microscopy and electron probe analysis. Following thermodynamic considerations were found to exert dominating influence on texture formation in copper electrocoats, namely grain boundary energy alone at the nucleation stage, and grain boundary energy on equal terms with bulk energy at the grain growth stage. Anisotropy of oriented structure was observed even at the texture formation onset and involved not only element size but also element shape. Thus for the major component the nuclei height was almost four times greater than the average of the two other dimensions. A comprehensive analysis of evolution of texture, substructure, microstructure and surface morphology in the course of copper layer growth revealed that the oriented structure of copper electrocoats features texture-related effects of anisotropy of substructure and nonhomogeneity of granular structure.

General Abstracts: Ferrous and Refractory Metals

Sponsored by: TMS

Program Organizers: Mark E. Schlesinger, University of Missouri, Department of Metallurgical Engineering, Rolla, MO 65409-0001 USA; Alton T. Tabereaux, Reynolds Metals Company, Smelter Technology Laboratory, Muscle Shoals, AL 35661-1258 USA; Dan J. Thoma, Los Alamos National Laboratory, Materials Science and Technology, Los Alamos, NM 87545-0001 USA; Patrice E.A. Turchi, Lawrence Livermore National Laboratory, Materials Science and Technology Division, Livermore, CA 94551 USA

Monday AM — Room: Canal A
March 13, 2000 — Location: Opryland Convention Center

Session Chair: George Spanos, Naval Research Laboratory, Washington, DC 20375-5000 USA

8:30 AM

Measurement of Burst Disc Properties Using Nanoindentation: *Neville R. Moody*[1]; Steven L. Robinson[1]; Mike Chiesa[1]; [1]Sandia National Laboratories, P.O. Box 969, MS9403, Livermore, CA 94551-0969 USA

Stainless steel burst discs are used in many high hydrogen pressure applications to insure safe operation. These discs are formed to a dome-like geometry and scored to produce a thin-walled, high strength ligament beneath the score. However, little is known about how structure and properties in this ligament control burst pressure. As a consequence we used nanoindentation to measure properties and finite element analysis to map stresses and strains in a 316L burst disc. The nanoindentation results showed a more than two-fold increase in strength due to scoring in good agreement with finite element results obtained using a strain hardening relationship to describe stresses in 316L. These results strongly suggest that the burst pressure is controlled by dislocation interactions. The test techniques and results will be discussed and used to show how a materials and mechanics approach can provide accurate measures of small volume properties.

8:50 AM

Void Nucleation at Inclusions in Ultra-High Strength Steels: *Luana E. Iorio*[1]; Warren M. Garrison[1]; [1]Carnegie Mellon University, Dept. of Matls. Sci. and Eng., Pittsburgh, PA 15213 USA

We have investigated the effects of carbon content on the strength and toughness of AF1410 type steels when the sulfur has been gettered as either chromium sulfide or as titanium carbosulfide. After tempering at 510°C for five hours the yield strengths were about 1500MPa, 1600MPa and 1710MPa for carbon levels of 0.16, 0.20 and 0.25wt.%, respectively. At a carbon level of 0.16wt.% the Charpy impact energy is about 180J when the sulfur is gettered as particles of titanium carbosulfide and about 100J when the sulfur is gettered as particles of chromium sulfide. As the carbon and yield strength increase the toughness decreases much more rapidly when the sulfur is gettered as titanium carbosulfide than when the sulfur is gettered as chromium sulfide which could be due to the void nucleation resistance of the titanium carbosulfide particles decreasing with increasing matrix strength while the particles of chromium sulfide have low resistance to void nucleation resistance at all strength levels. In this work the void nucleation resistance has been determined for titanium carbosulfide and chromium sulfide particles at strength levels ranging from about 1500MPa to 1710MPa. This work was funded by the Division of Materials Research of the National Science Foundation.

9:10 AM

Use of Metallic-Glasses in MoSi2-Stainless Steel Joining: *Rajendra U. Vaidya*[1]; Partha Rangaswamy[1]; [1]Los Alamos National Laboratory, MST-6, MS G770, Los Alamos, NM 87545 USA

Residual stresses due to mismatch in elastic and thermal expansion properties in ceramic-metal joints can lead to failure at the interface or within the brittle ceramic. Low temperature brazing techniques coupled with ductile interlayers alleviate this problem. However, the use of precious metal based brazes and the incorporation of the interlayer add to the complexity and cost of the joining process. We have overcome these problems with the use of metallic-glass brazes. This is a new idea that eliminates the need for separate interlayers in ceramic-metal joining. We present the results of our preliminary joining experiments using metallic-glasses. Stainless steel 316L and molybdenum disilicide were successfully brazed using a cobalt based metallic glass. Issues pertaining to the interfacial chemistry, joint strength and residual stresses are presented here.

9:30 AM

Stress-Rupture Strength and Creep Behaviour on Molybdenum-Rhenium Alloys: *Bernd Fischer*[1]; Dietmar Freund[1]; Samantha Baxter[1]; Jan-C Carlen[2]; Todd A. Leonhardt[2]; [1]Fachhochschule Jena, Dept. of Matls. Tech., Univ. of Appl. Sci., Jena D-07745 Germany; [2]Rhenium Alloys Inc., P.O. Box 245, Elyria, OH 44036-0245 USA

Due to the outstanding properties of molybdenum and rhenium, which have very high melting points and excellent strength at elevated temperatures, molybdenum-rhenium alloys are valuable materials in applications where high strength at high temperature is required. The manufacturing processes of Mo-Re alloys can be tailored so as to enhance the mechanical properties of the part. The design engineer and manufacturer need exact information on the creep behavior, and stress-rupture strength at elevated temperatures. After an extensive literature search of the technical literature, relatively few reports were found on the mechanical properties of molybdenum-rhenium alloys, so an investigation was set forth using a special test facility for measuring high melting materials at temperatures up to 3273K under a protective atmosphere. The stress-rupture diagrams were determined for the molybdenum-rhenium alloys with rhenium contents between 41 and 51 weight percent at test temperatures of 1473K, 1873K and 2273K at 0.1 to 10 hours creep rupture times.

9:50 AM

Effect of the Carbide Solution Heat Treatment of ASTM-75 Alloys on the Wearing Behavior of the UHMWPE Material: *Edgar Guerra Martinez*[1]; H. M. Mancha[1]; A.J. U. Perez[2]; H. Lopez[3]; [1]Centro de Investigacion y Estudios Avanzados del IPN, Tribology, Carr. Saltillo-Monterrey Km 13, P.O. Box 663, Saltillo, Coahuila 25000 Mexico; [2]Universidad Autonoma de Nuevo Leon, Monterrey, NL; [3]University of Wisconsin, Milwaukee, WI USA

Today, one of the most important problems that face metallic hip and knee prostheses researching is the wear of polymeric and metallic materials used manufacture orthopedic implants to rehabilitate patients with no longer functional joints. The aim of this researching work was to study the effect of some surface modifications on an ASTM-F75 alloy on the wear rate of UHMWPE in order to decrease the amount of particles produced by sliding of the metal against the polymer. The desired amount of particles being that which can be removed via the patient lymphatic system. To study the wear properties, specimens of ASTM-F75 alloy were prepared by precision investment casting process, surface treated, and tested against UHMWPE at 37°C, applying two types of lubricant solutions (distilled water and Ringer solution).

10:10 AM Break

10:30 AM

Microstructure and Impact Toughness of Heat Affected Zones of an SA 508 Steel: *Sangho Kim*[1]; Sunghak Lee[1]; Soon Ju Kwon[1]; Joo Hag Kim[2]; Jun Hwa Hong[2]; Nack Joon Kim[1]; [1]Pohang University of Science and Technology, Matls. Sci. and Eng., San 31 Hyoja-dong, Nam-gu, Pohang, Kyoungbuk 790-784 Korea; [2]Korea Atomic Energy Research Institute, Nuclear Matls.Tech. Dev., Dajeon 305-600 Korea

In this study, microstructures of a heat affected zone (HAZ) of an SA 508 steel were identified by Mossbauer spectroscopy in conjunction with microscopic observations, and were correlated with impact toughness. Specimens with the peak temperature raised to 1350°C showed mostly martensite. With the peak temperature raised to 900°C, the martensite fraction was reduced, while bainite or martensite island were formed because of decrease in a prior austenite grain size and the slow cooling rate from the lower austenite region. As the martensite fraction increased, hardness and strengths tended to increase, whereas impact toughness decreased. However, impact toughness of the subcritical HAZ with the peak temperature raised to 650°C-700°C was seriously reduced after post-weld heat-treatment (PWHT) since carbide particles were of primary importance in initiating voids.

10:50 AM

Nanocomposite Magnets: *D. J. Branagan*[1]; [1]Bechtel BWXT Idaho LLC, Idaho Nat. Eng. and Environ. Lab., 2351 N. Blvd., Idaho Falls, ID 83415-2218 USA

The realization of high energy densities in permanent magnetic materials requires careful control of both the composition and the processing conditions in order to develop appropriate microstructures capable of storing high energy densities. It will be shown that nanoscale metal matrix composite microstructures can be developed in modified Nd-Fe-B alloys by careful selection, manipulation, and control of the alloying elements. The development of composite microstructures in hard magnetic materials is a novel approach resulting in many beneficial effects on the resulting structure/processing/property relationships

General Abstracts: Materials Processing and Fundamentals

Sponsored by: TMS

Program Organizers: Mark E. Schlesinger, University of Missouri, Department of Metallurgical Engineering, Rolla, MO 65409-0001 USA; Alton T. Tabereaux, Reynolds Metals Company, Smelter Technology Laboratory, Muscle Shoals, AL 35661-1258 USA; Dan J. Thoma, Los Alamos National Laboratory, Materials Science and Technology, Los Alamos, NM 87545-0001 USA; Patrice E.A. Turchi, Lawrence Livermore National Laboratory, Materials Science and Technology Division, Livermore, CA 94551 USA

Monday AM — Room: Canal E
March 13, 2000 — Location: Opryland Convention Center

Session Chair: A. K. Vasudevan, Office of Naval Research, Code 332, Arlington, VA 22217-5660 USA

8:30 AM

Experimental Comparison of the Intrinsic Jump Frequency Formalism with the Traditional Darken-Manning Formalism for Describing Diffusion in Cu-Ni-Zn: *Robert T. DeHoff*[1]; Nagraj Kulkarni[1]; [1]University of Florida, Dept. of Matls. Sci. and Eng., Gainesville, FL 32611 USA

Earlier presentations derived the following expression for the intrinsic flux of component k in a multicomponent system: where Ck is the molar concentration of component k, ÿk is the composition dependent jump frequency of component k determined in a tracer diffusion experiment, ÿ is the jump distance and ÿk is a factor that reports the extent to which the atom jumps are biased. All of the information in this equation is determinable from independent experiments except ÿk. The traditional Darken-Manning approach to the description of multicomponent diffusion uses tracer diffusion coefficients, thermodynamic information and a contribution derived from the vacancy wind effect to compute intrinsic diffusion coefficients in the phenomenological description of the diffusion process. In this presentation these two disparate descriptions have been used to compute the ex-

perimental observables in a diffusion experiment (composition paths and profiles, Kirkendall shifts) for the system Cu-Ni-Zn. A simulation based upon these sets of equations permits separate computation of the experimental observables with each of the various influences assumed to operate in each formalism. This allows a definitive assessment of the effect that each of these factors has in predicting the experimental observables and a definitive comparison of the two approaches.

8:50 AM

Asymptotic Decay Analysis of Phase Coarsening Data: *Steven P. Marsh*[1]; [1]Naval Research Laboratory, Code 6325, 4555 Overlook Ave. SW, Washington, DC 20375-5343 USA

The progress of phase coarsening is generally quantified by the increase in the average particle size. However, coarsening is essentially a relaxation process driven by a reduction in the excess interfacial energy of a multiphase structure. Analysis of coarsening data via the decay of a global property, such as specific surface area, introduces a non-arbitrary temporal parameter that relates the experimental clock to an asymptotic time scale. This approach permits the fitting of data at earlier times, where the driving force is greatest, and more accurate determination of the power-law rate constant. Implications of this approach on measurement and interpretation of coarsening kinetics will be discussed.

9:10 AM +

Microstructural Evolution of Solid-Liquid Mixtures: *Victoria A. Snyder*[1]; Jens Alkemper[1]; Peter W. Voorhees[1]; [1]Northwestern University, Matls. Sci. & Eng., 2225 N. Campus Dr., Evanston, IL 60208-3108 USA

The coarsening of solid Sn particles in a Pb-Sn eutectic liquid was studied under microgravity conditions during the Microgravity Science Laboratory-1 mission. A clustered structure of particles exists at the beginning of the experiment for samples containing 10% and 20% volume fractions of coarsening phase. The coarsening of such a clustered structure of particles was studied via numerical simulations of coarsening using the approach developed by Akaiwa and Voorhees. Theoretically predicted particle size distributions and spatial correlation functions will be directly compared to the results from the spaceflight experiment. Furthermore, the microstructure in samples containing 50% and 70% coarsening phase (where a percolated structure of particles is present) was examined in orientation space using orientation imaging microscopy. Electron back-scattered diffraction patterns were used to determine the misorientation between contacting particles as well as the evolution of the misorientation distribution function with coarsening time.

9:30 AM

Elevated Temperature Mechanical Properties and Microstructure of a Ag-Cu-In-Ti Active Metal Braze Alloy: *John J. Stephens*[1]; Thomas E. Buchheit[1]; [1]Sandia National Laboratories, Matls. Joining Dept., P.O. Box 5800, MS0367, Albuquerque, NM 87185-0367 USA

Commercial Ag-Cu-In-Ti active metal braze alloys such as Incusil ABA (TM of WESGO Metals, Inc.) are attractive for metal-ceramic brazing applications because they eliminate the need for metallization of the ceramic and have relatively low braze process temperatures (~750°C). We have studied the elevated temperature mechanical properties of Incusil ABA using compression testing over the temperature range 150-550°C. For the case of constant load creep data, the minimum strain rate as a function of stress and temperature can be represented by the Garofalo sinh equation. Based on compressive stress-strain results, the 0.2% offset yield stress and work-hardening slope for this alloy are observed to have a maximum in the temperature range of 100-150°C. This effect is discussed in view of the microstructure of this alloy, which contains a significant volume fraction of Cu2InTi ordered intermetallic compound. Low force nanoindentation test results will be presented which quantify the relative hardness of this phase compared to the Cu-rich phase and the Ag-rich matrix of this braze alloy. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the U.S. Dept. of Energy under contract DE-AC04-94Al85000.

9:50 AM

Thin Film Coated Glass Soldering: *F. Michael Hosking*[1]; [1]Sandia National Laboratories, Dept. 1833, P.O. Box 5800, MS0367, Albuquerque, NM 87109-0367 USA

Conductive adhesives and solders are generally used to join soda-lime glass to itself and other materials. Soldering usually requires metallization of the glass. Two thin film glass coatings, Cr-Pd-Au and Cr-Ni-Sn, were investigated. Glass-to-glass test specimens, metallized with Cr-Pd-Au and soldered with 60Sn40Pb solder, had shear strengths approaching 16.5 MPa. Similar Cr-Ni-Sn coated specimens gave higher strengths, 20-22.5 MPa, with failures primarily in the glass. Surface roughness of the glass pieces also affected the coating uniformity and bond strength. Solder wetting and shear test results are discussed. The work was conducted at Sandia National Laboratories, a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000.

10:10 AM

Preparation of Silica Fibers from a Suspension: *Hiroyuki Nakamura*[1]; Akira Shimizu[2]; Yoko Suyama[2]; Eiichi Abe[1]; Noriyuki Yamada[1]; [1]Kyushu National Industrial Research Institute, Dept. of Inorganic Matls., 807-1, Shuku, Tosu, Saga 841-0052 Japan; [2]Shimane University, Dept. Matl. Sci., 1060, Nishikawazu, Matue, Shimane 690-8504 Japan

Fibrous silica was prepared by drying silica particle suspension. The silica fibers were obtained only on walls, which were wetted well by the suspension. The fibers were made of roughly close-packed silica particles. Widths of the fibers were affected by some preparation conditions. In this study, wider fibers were obtained under these conditions: higher silica particles concentration, larger particle diameter, and lower drying temperature. From an observation of a generation of fibers, the formation mechanism was considered as following; When a dispersion of silica was dried, a silica film made of silica particles were generated on a wall. During drying, since the shrinkage ratio of the film depends on the distance from the surface of the suspension, stress whose direction is parallel to the suspension surface arises. Because of the horizontal stress, the cracks are considered to proceed to the downward to generate silica fibers.

10:30 AM Break

10:50 AM

Formation of Cu-Ni-Zr Amorphous Powders with Significant Supercooled Liquid Region by Mechanical Alloying Technique: *Pee Yew Lee*[1]; Chung Kwei Lin[2]; G. S. Chen[2]; [1]National Taiwan Ocean University, Instit. of Matls. Eng., 2 Pei-Ning Rd., Keelung 202 Taiwan; [2]Feng-Chia University, Matls. Sci., Taichung 400 Taiwan

Recently, the studies on amorphous alloys were focused on the formation of bulk amorphous with a distinct supercooled liquid regions by using the traditional melt quenching technique, even water quenching are quite active. However, the composition of the material for the production of bulk amorphous alloys by quenching method is limited by the necessary low cooling rate. Changes in composition, therefore, strongly affect the glass forming ability and hence the required cooling rates to obtain bulk amorphous samples. In comparison to quenching techniques, amorphization by mechanical alloying process offers an alternative way which might be a promising method for the formation of a bulk amorphous with an obvious supercooled liquid region through the powder metallurgy route. In this study, we have investigated the possibility of preparing amorphous Cu-Ni-Zr powders by mechanical alloying. The results indicated that several amorphous alloy samples were found to exhibit a wide supercooled liquid region before crystallization. This is believed to be the first evidence for the appearance of a supercooled liquid region for mechanically alloyed Cu-Ni-Zr amorphous powders. The origin of the significant supercooled liquid region of these new alloys is discussed.

11:10 AM

A Thermodynamic Model for Mechanical Alloying: *Saheb Nouari*[1]; Abdul Razak Daud[1]; Shahidan Radiman[2]; Redzuwan Yahaya[2]; [1]University Kebangsaan Malaysia, Dept. of Matls. Sci., Faculty of Physical and Appl. Sci., Bangi, Selangor 43600 Malaysia; [2]University

Kebangsaan Malaysia, Dept. of Nuclear Sci., Faculty of Physical and Appl. Sci., Bangi, Selangor 43600 Malaysia

Mechanical alloying is a useful technique to produce different materials. Despite it's importance a few attempts has been made to model the fundamental process on one hand and to explain thermodynamically the mechanism of mechanical alloying on the other hand. In the present study, an attempt to develop a thermodynamic model for solid solution formation by mechanical alloying is presented. The main objective of the work is to describe from a purely thermodynamic point of view the evolution of solution during mechanical alloying based on the regular solid solution model, taking in to account the energy rise during alloying due to the generation of different defects.

11:30 AM

A Study of Casting Filling Process Using Simulation Tools: *Pongsakd Dulyapraphant*[1]; Patcharin Poosanaas[1]; Supparit Lounkosonchai[1]; Harit Sutabutr[1]; Panya Srichandr[1]; [1]National Metal and Materials Technology Center, Manufacturing and Design Tech. Ctr., 9th Floor, Gypsum Metropolitan Bldg., 539/2 Sri-Ayudhya Rd., Bangkok 10400 Thailand

The application of computer simulation are being widely used and becoming extremely beneficial in improving casting process and in tooling design. The use of simulation provides an insight into how each process related parameters affecting the quality of the casting. In this study, the influence of filling process on the quality of casting will be investigated by using a casting simulation package. Different types of gating systems will be simulated in order to identify how each component of the gating system contribute to the filling process. The comparison between simulation results and experimental results will be presented in order to verify the simulation results. Furthermore the use of simulation results to detect some flow related defects will be studied as well.

11:50 AM

The Story of the Safety Related Problems in the Titanium Industry in the Last Millennium: *Eldon R. Poulsen*[1]; [1]TI + MG Consultant, 4360 Malaga Dr., Las Vegas, NV 89121 USA

The titanium industry dates back to the turn of the century. The actual commercial production of the metal actually started in about 1950. By the end of the century, the industry was producing at the rate of over 100-million pounds per year. From a safety standpoint, the best judge of the industry is to evaluate each of the fatalities that have been experienced during the last 50 years. These as well as other major safety related problems such as fires will be discussed. Early on the problems was lack of knowledge with regards to furnace design and related explosions. The knowledge at the time was based on steel technology. The addition of the problem of hydrogen explosions was a totally new problem. When molten titanium reacts with water, the water breaks down and liberates the hydrogen which results in major explosions. During the first 5 years of the industry, furnace explosions killed a total of 6 employees. The next problem that plagued the industry was that of fires and explosions from sponge and fines fires. Fines fires and explosions killed a total of 3 employees. The third problem was confined space entry. Fatalities resulted from argon, nitrogen, and other inert gases. A total of 5 fatalities have been recorded to date from these causes. This paper discusses each of the fatal incidents and explains the cause and effect. Safety committees were formed and safe operating equipment and procedures were developed. Three separate lists of safety recommendations are included, var furnace design and operation, handling and storage of titanium fines and sponge and confined space entry based on OSHA standards.

General Non-Ferrous Pyrometallurgy: Industrial Operations and Recycling

Sponsored by: Extraction & Processing Division, Pyrometallurgy Committee

Program Organizers: Robert L. Stephens, Cominco Research, Trail, British Columbia V1R 4S4 Canada; Pekka Taskinen, Outokumpu Research Oy, Pori FIN-28101 Finland

Monday AM — Room: Bayou B
March 13, 2000 — Location: Opryland Convention Center

Session Chair: Robert L. Stephens, Cominco Research, Trail, British Columbia V1R 4S4 Canada

8:30 AM

The Use of Ausmelt Technology at the Minsur Tin Smelter and Refinery: *Colette M. Ng*[1]; Ken R. Robilliard[2]; [1]Ausmelt Limited, 12 Kitchen Rd., Dandenong, Victoria 3715 Australia; [2]Funsur S.A., KM 240 Panamericana Sur, Pisco-Ica, Peru

The Peru-based tin mining company, Minsur S.A., commissioned Ausmelt Limited to design, supervise construction, and commission a tin smelter and refinery for production of refined tin metal. The plant is located 240 km south of Lima, near Pisco, Peru, and is operated by Funsur S.A., a wholly-owned subsidiary of Minsur. Selection of Ausmelt Technology followed a series of crucible scale test work and pilot plant trials conducted at Ausmelt's facility in Dandenong, Australia and two feasibility studies undertaken by Ausmelt in 1991 and 1993. Ausmelt began the plant design in 1994 with the construction phase following in 1995. Commissioning of the plant commenced early in 1996 with a Phase 1 target throughput of 30,000 tonnes per annum of concentrates. In mid-1998, oxygen enrichment of the Ausmelt lance air was introduced to expand the capacity to the Phase 2 throughput of 40,000 tonnes per annum of concentrates. The process route involves the use of an Ausmelt furnace for primary concentrate smelting, followed by a conventional tin pyro-refining circuit to produce high-grade tin suitable for sale. Further work continues between Ausmelt and Funsur to investigate the use of an alternative, more economical fuel source and the installation of a second Ausmelt furnace. This paper reviews the project to date with details of ongoing operations and developments at the Minsur Tin Smelter.

8:55 AM

Treatment of Industrial Waste in Reverberatory Furnace at Onahama Smelter: *Takayuki Sato*[1]; Nobuo Kikumoto[1]; Kiyotaka Abe[1]; Michio Nishiwaki[1]; [1]Onahama Smelting & Refining Company Limited, Smelting, 1-1 Nagisa Onahama, Iwaki, Fukushima 971-8101 Japan

Recently, the treatment of industrial waste materials has been a serious social problem here in Japan. Landfilling is now strictly prohibited due to a limited land area and incineration method is also regulated so as to not generate dioxins and furans (DXN). With this background, Onahama Smelter has begun to treat automobile shredder dust in reverberatory furnaces to recover various metals such as copper, gold, silver and palladium without generation of DXN. The total volume of these dusts is expected to be more than 1 million metric tonnes a year in Japan. Onahama Smelter is now planning to treat about 20% of them in the near future by using tonnage oxygen. In this paper, the heat balance and control method of DXN in reverberatory furnaces and treatment of these dusts are described.

9:20 AM

Precursors for PCDD/F Formation During Combustion of Electronic Scrap: *Menad Nourreddine*[1]; [1]Luleå University of Technology, Div. of Process Metallu., Luleå Se-97187 Sweden

The flame retardant contained in the electronic scrap can form dioxins (PCDDs) and furans (PCDFs). Their formation can be dependent on the quantities of carbon, hydrogen, chlorine, and oxygen present in a given system, as well as on parameters such as temperature

and pressure. Inadequate supply of combustion air (incomplete oxidation), low combustion temperatures (incomplete combustion), and insufficient turbulence in the combustion are factors which can favour their formation. Dioxins and furnans were also produced calatytically from chlorinated phenol precursors, non-chlorinated compounds that were chemically modified, and reaction of phenol with inorganic chloride. In this paper, different precursors such as combinations of C, H, O, Cl, rapid formation/combustion intermediates, and routes to PCDD/Fs are reviewed, and the influence of the amount of PVC on the formation of these isomers is discussed.

9:45 AM

Synergetic Effects During Phosphorous Production in Submerged-Arc Furnaces: *Markus A. Reuter*[1]; Diekske van der Pas[1]; Rob de Ruiter[2]; [1]Delft University of Technology, Faculty of Appl. Earth Sci., Mijnbiuwstraat 120, Delft, The Netherlands; [2]Thermphos, Postbus 65, Vlissingen, The Netherlands

In this paper, the kinetics of phosphorous production in submerged-arc furnaces will be discussed as a function of temperature, as well as various ore and reductant types. Interesting positive synergetic effects on the rate of reaction could be observed when mixing different types of ores. The results will be discussed with reference to a kinetic model, microprobe analyses, etc. The effects these results have on the control of the furnace will also be discussed in detail, indicating how these could be incorporated into the electrode and metallurgical control systems for submerged arc-furnaces.

10:10 AM Break

10:25 AM

Peirce-Smith Converter Hood Design Analysis Using Computational Fluid Dynamics Modeling: *Paykan Safe*[1]; [1]Gas Cleaing Technologies Inc., 4950 North O'Connor Rd., Ste. 250, Irving, TX 75062 USA

Computational fluid dynamics (CFD) modeling provides a powerful tool to assist with the design of ventilation and fume control systems in smelters and other high temperature metallurgical facilities. For this paper, this tool has been used to analyze the off-gas flow patterns exiting the mouth of a Peirce-Smith converter into a water-cooled hood and drop out box. The effects of various process and physical plant design parameters on process gas and fume capture and potential build up on the converter hoods was examined, and the optimum design and operating parameters were determined.

10:50 AM

Process Control Improvements at the Kennecott Utah Copper Smelter: *Robert M. Leary*[1]; Marielle A.S. Siraa[2]; [1]Kennecott Utah Copper Corporation, Smelter, P.O. Box 329, 12000 W. 2100 S., Magna, UT 84044 USA; [2]Rio Tinto plc, Tech. Svcs. Ltd., P.O. Box 50, Castlemead Lower Castle St., Bristol, England BS997YR UK

The Kennecott Utah Copper Smelter operates two Outokumpu flash furnaces: a smelting furnace for production of high-grade matte and a converting furnace for production of blister copper. Flash furnaces typically possess several characteristic features that must be considered in process control development such as long lag times associated with settler volume, non-linear input and output responses, large process gains, and unmeasured disturbances. Additionally, the Kennecott smelter possesses certain unique characteristics which must be considered such as a single mine concentrate source, small concentrate blending capacity, feed preparation facilities that introduce significant lags between furnace control parameters and manipulated set points and converter slag chemistry. In order to improve furnace control and on-line time, a process control system was developed which features feed forward and feed back control. The feed forward control module is based on a steady-state heat and mass balance that is executed in response to furnace feed changes. The feed back control module is based on Proportional-Integral control equations that were developed by statistical inference and are executed in response to furnace product grade and temperature deviations from set point. To provide regular feed back information to the control room operators, new sampling methods were developed which allow the operators to obtain molten metal samples at hourly intervals and allow for rapid laboratory turn around. The control system was implemented in May 1999 and a review of it's operation, adjustments, and future work will be discussed.

11:15 AM

Reversing the Philosopher's Stone: Recovering Iron from Copper Slags and Residues (Adeptus Ineptus): *Larry M. Southwick*[1]; [1]L. M. Southwick and Associates, 992 Marion Ave., Ste. 306, Cincinnati, OH 45229 USA

Interest has been expressed over the years in recovering iron from copper smelting and leaching residues. In the United States, this interest resulted in commercial operations and pilot plant tests by, among others, Lakeshore Copper on leaching residues, Phelps Dodge on copper matte, United Verde on granulated slag, and the USBM on molten slag. In most case, these were directed at producing sponge iron suitable for cementation of copper from spent leach solutions. Cementation of copper on iron from acid mine drainage solutions in the "Alchemists' Age" is likely what gave rise to mythical stories of a "Philosopher's Stone". While none of the above facilities continue in operation nor is cementation of great interest in current flowsheets, there does remain the need to treat acidic mine and tailing pond drainage. In a related field, there has also been increasing interest within the steel industry to recover iron from various steel plant iron oxide wastes to supplement a tightening supply of pig iron and scrap. Many steel waste plants propose to use technologies and processing concepts similar to those practiced earlier on the copper industry. This paper will review the processes and designs used to make sponge iron from copper residues, identify the factors that led to success or failure in these approaches, and then apply those results to evaluate potential operating difficulties with the technologies being proposed and installed for steel plant wastes. While there has been no visible effort to cross-fertilize technologies between the ferrous and non-ferrous industries in this field, this paper will identify where such information transfer may be desirable.

11:45 AM

The Case for the Copper Mini Smelter: *Rolf J. Wesley*[1]; [1]Kvaerner Metals, 12657 Alcosta Blvd., San Ramon, CA 94583 USA

In recent years the trend in Copper smelting has been to expand existing smelters to increase their throughput. New smelters that are being considered are very large. Despite this trend to larger smelters, there are still a number of conditions where a small smelter can be economically viable. The paper examines these conditions and outlines the process concepts for a small smelter. The paper outlines several options for treatment methods and presents a summary of the economic conditions that would lead to a successful small smelter project.

High-Temperature Superconductors: BSCCO Tapes & Applications

Sponsored by: Electronic, Magnetic & Photonic Materials Division, Structural Materials Division, Superconducting Materials Committee

Program Organizers: U. Balu Balachandran, Argonne National Laboratory, Argonne, IL 60439 USA; Pradeep Haldar, Intermagnetics General Corporation, Latham, NY 12110-0461 USA; Chandra Pande, Naval Research Laboratory, Materials Science and Technology Division, Washington, DC 20375-5000 USA

Monday AM — Room: Canal D
March 13, 2000 — Location: Opryland Convention Center

Session Chair: U. (Balu) Balachandran, Argonne National Laboratory, Ceramics Section, Argonne, IL 60439 USA

8:30 AM Invited

High-Tc Conductor Development for Use in Electric Power Devices: *Heinz-Werner Neumueller*[1]; [1]Siemens AG, ZT EN4, P.O. Box 3220, Erlangen D-91050 Germany

Demonstration of HTS technology in power systems requires development of practical and robust conductors on technical scale. Meanwhile several manufacturers offer elementary conductors like 2223 tapes having reasonable engineering current densities in quantities sufficient for the manufacturing of representative power devices like transformers and current limiters for use in first pilot systems. Similar to the LTS conductor development the realization of larger high current HTS power devices need advanced cabled conductors designed for AC-application. Robel bars have been manufactured consisting up to 13 tapes of BPSCCO 2223 multifilamentary tapes. The production line delivers the conductor material for the low voltage winding of the 1 MVA railway model transformer currently being under construction and avoids complicated and expensive coil winding. In course of the resistive fault current limiter development a continuous production of switching elements has been established. Design considerations, quality measures and test results of the 1 MVA model will be presented.

9:10 AM Invited

Fatigue Behavior of Multifilamentary BSCCO Wire Used in Superconducting Ac Motors for Navy Ship Propulsion: *Donald U. Gubser*[1]; [1]Naval Research Laboratory, Matls. Sci. and Tech. Div., Code 6300, 4555 Overlook Ave. S.W., Washington, DC 20375 USA

A new type of ac superconducting motor is under development for the US Navy. This motor uses BSCCO conductor, wound into racetrack magnets, mounted on the rotor. Such magnets will be subjected to considerable cyclic stress, both during operation and during thermal cycling. It is well known that a monotonic strain of more than a few tenths of a percent can degrade the critical current in high temperature superconductor wires. A much lower strain, if applied repeatedly, also can degrade the critical current through cumulative damage effects. The possible fatigue damage of HTS wires is a significant concern for the reliability and service life issues in the development of motors and other power equipment. We report on measurements of the critical current fatigue in commercial BSCCO/Ag multi-filamentary wires. Long (250 mm) length sections of the wire were measured in liquid nitrogen using a conventional servo-hydraulic mechanical test system and with sinusoidal loading at a frequency of 10 Hz and zero load ratio. Strain ranges were from 0.01 to 1.0 percent. Critical current failure, using a stringent 0.1 microvolt-centimeter field criteria, was measured as a function of the number of load cycles at each strain level. The fatigue limit is determined from the strain-life curves. The relationship of the fatigue limit to the monotonic critical strain is discussed. In addition, systems advantages of superconducting motors for Navy ships will be discussed. Work is supported by the Office of Naval Research.

9:50 AM Break

10:00 AM

Grain Morphology of High Tc Superconducting Wires for Superconducting Motors: *C. S. Pande*[1]; K. L. Zeisler-Mashl[1]; R. A. Masumura[1]; [1]Naval Research Laboratory, Matls. Sci. Div., Washington, DC 20375 USA

Superconducting properties of practical high Tc superconductors are strongly influenced by their grain morphology. Towards this goal, texture measurements were conducted for BSCCO 2212 (Bismuth-Strontium-Calcium-Copper Oxide) tapes made by dip coating or by powder-in-tube techniques. BSCCO 2212 grain texture measurement was performed for both c-axis using (001) pole figures from (008) reflections and a-b axes using (115) pole figures. Current transport properties of these tapes were also measured and correlated with texture parameters obtained from contours of the texture plots. Grain morphology was inferred from the texture plots and was found to be consistent with a model based on global alignment of the c-axis and the presence of colonies of grains differing mostly in c-axis twist. There is a good correlation between the c-axis texture and Jc. Surprisingly on a global basis the system showed little a-b texture. However the material did give indications of local a-b texture in addition to the c-axis texture. These results far as the grain morphology is concerned can be explained in terms of colonies of grains. Inside a typical colony, the grains differ mostly in their small amount of twist along c-axis. These colonies are connected by complicated grain boundary structures.

10:40 AM

Histographic Analysis of the Microstructure of Ag/Bi-2223 Composite Conductors*: *Roxanne Baurceanu*[1]; Nazarali N. Merchant[1]; Albert K. Fischer[1]; Victor A. Maroni[1]; Ronald D. Parrella[2]; [1]Argonne National Laboratory, Chem.Tech. Div., 9700 S. Cass Ave., Argonne, IL 60439 USA; [2]American Superconductor, Two Technology Dr., Westborough, MA 01581 USA

A group of procedures has been developed to identify, quantify (in terms of area fraction), and spatially map the nonsuperconducting second phases (NSPs) that are formed during heat treatment of Ag/Bi-2223 multifilament composite conductors. These procedures involve (1) extracting the gray scale histogram from scanning electron microscope images of transverse cross sections of Ag/Bi-2223 after varying degrees of thermal treatment, (2) correlating selected ranges of gray scale values with the energy dispersive x-ray scans of those regions (to obtain metallic element ratios), (3) performing Raman microscopy analyses of the same regions (to identify the phases present), and (4) making systematic measurements of the Bi-2223 grain colony size and texture factor as they relate to NSP size, content, and composition. From these results we have developed quantitative correlations between key heat treatment parameters (such as, temperature, oxygen partial pressure, and treatment time) and the chemical form of the NSPs, their size distributions, their area fractions, and their impact on the final microstructure of the filaments. We find that oxygen partial pressures and temperatures on the high end of the Bi-2223 stability range tend to encourage the formation of the 14/24 alkaline earth cuprate, whereas oxygen partial pressures and temperatures on the low end of that range tend to encourage the 2/1 alkaline earth cuprate. The quality of the Bi-2223 grain colony microstructure is most sensitive to heat treatment temperature and the presence of large NSPs. The optimum temperature for achieving a robust grain colony microstructure tends to increase with increasing oxygen partial pressure. *Work sponsored by the U.S. Department of Energy, Energy Efficiency and Renewable Energy, as part of a DOE program to develop electric power technology, under Contact W-31-109-ENG-38.

11:20 AM Invited

Development of Bi-2212/Ag Conductors and Coils: *Hiroaki Kumakura*[1]; Hitoshi Kitaguchi[1]; Hanping Miao[1]; Kazumasa Togano[1]; Tsutomu Koizumi[2]; Nozomi Ohtani[2]; Takayo Hasegawa[2]; Katsumi Ohata[3]; Junichi Sato[3]; Kazuhide Tanaka[4]; Michiya Okada[4]; [1]National Research Institute for Metals, 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047 Japan; [2]Showa Electric Wire & Cable, 2-1-1 Odasakae, Kawasaki, Kanagawa 210-8660 Japan; [3]Hitachi Cable Limited, 3550 Kidamari, Tsuchiura, Ibaraki 300-0026 Japan; [4]Hitachi Limited, 7-1-1 Ohmika, Hitachi, Ibaraki 319-1292 Japan

Development of two types of Bi-2212/Ag superconductors with excellent current carrying capacities is now in progress. One is a surface-coated multilayer tape conductor prepared by applying Pre-Annealing and Intermediate Rolling (PAIR process) before a heat treatment. The other is Bi-2212 multifilamentary wires fabricated by applying Rotation Symmetric Arranged Tape-in-tube (ROSAT process, where Bi-2212 tapes were arranged with triple rotation symmetry. We evaluated current carrying characteristics of these Bi-2212 conductors at various temperatures and fields. Excellent Ic and Jc values of about 380A and 2?~105A/cm2 were obtained in a field of 30T at 4.2K for short tapes cut from the PAIR processed 100m tape. E(electric field)-J(current density) characteristics was also improved by the PAIR process. Jc values of pancake coils prepared with 100m-class PAIR processed tapes were much higher than those of the no-PAIR processed tape. The ROSAT wires show very small Jc anisotropy with respect to the field orientation in spite of excellent Jc values. A 990-filament wire showed Ic and Jc of 360A and 105A/cm2 in 28T at 4.2K. Recently, we fabricated 400m-length ROSAT wires, and constructed a solenoid magnet using these wires. Test result of the magnet will be reported.

International Symposium on Iridium: Mechanical Properties

Sponsored by: Structural Materials Division, Refractory Metals Committee

Program Organizers: Evan K. Ohriner, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6083 USA; H. Harada, National Research Institute for Metals, Tsukuba, Ibaraki 305 Japan; R. D. Lanam, Engelhard-CLAL, Careret, NJ 07008 USA; Peter Panfilov, Ural State University, Ekatrinburg 62001 Russia

Monday AM — Room: Jackson A/B
March 13, 2000 — Location: Opryland Convention Center

Session Chairs: Evan K. Ohriner, Oak Ridge National Laboratory, Metals and Ceramics Division, Oak Ridge, TN 37831-6083 USA; William J. Barnett, U.S. Department of Energy, Office of Space and Defense Power Systems, Germantown, MD 20874-1290 USA

8:30 AM Invited

Micro- and Macro-Alloying of Ir-Base Alloys: E. P. George[1]; *C. T. Liu*[1]; [1]Oak Ridge National Laboratory, Mets. and Cer. Div., P.O. Box 2008, Oak Ridge, TN 37830-6115 USA

Ir-base alloys are of interest for structural applications at high temperatures because of their high melting point (2443°C) and good oxidation and corrosion resistance. A major concern for structural use is their low tensile ductilities when tested at conventional strain rates at ambient temperatures and at high strain rates at elevated temperatures. Microalloying has been used to strengthen grain boundaries and suppress brittle intergranular fracture in Ir alloys. Auger studies indicate that Th has a strong tendency to segregate to Ir grain boundaries and suppress intergranular fracture at elevated temperatures. Among macroalloying elements, Hf is found to be the most effective in improving the strength of Ir alloys at room and elevated temperatures. Ir-W alloys doped with Th have been successfully developed as cladding materials for space power applications at temperatures to 1400°C. The current studies of Ir-base γ-γ alloys and intermetallic alloys will be also briefly reviewed.

9:00 AM

Comparing Experimental Measurements with Ab Initio Simulations of the Elastic and Plastic Behavior of Single Crystalline Iridium: *T. J. Balk*[1]; O. N. Mryasov[2]; Y. N. Gornostyrev[3]; P. Panfilov[4]; A. J. Freeman[2]; K. J. Hemker[1]; [1]Johns Hopkins University, Dept. of Mech. Eng., 200 Latrobe Hall, 3400 N. Charles St., Baltimore, MD 21218 USA; [2]Northwestern University, Dept. of Physics and Astronomy, Rm. F275, 2145 No. Sheridan Rd., Evanston, IL 60208-3112 USA; [3]Instit. of Metal Physics, 18 S. Kovalevskaya St., Ekaterinburg 620219 Russia; [4]Urals State University, Instit. of Physics and Appl. Math., Ekaterinburg 620083 Russia

Iridium is one of two face-centered cubic (FCC) metals that is known to undergo brittle fracture, in stark contrast with the normal ductile failure of other FCC metals. The occurrence of brittle fracture, which follows significant plastic deformation of up to 70%, is thought to result from the energetics of the dislocation core. Ab initio first-principles methods have been used to predict fundamental characteristics that govern the mechanical behavior of iridium, e.g., elastic constants, dislocation structure and fracture parameters such as surface and unstable stacking energies. The elastic behavior and strength of single crystalline iridium have been measured experimentally. These measurements and transmission electron microscopy (TEM) observations of the dislocation core structure will be compared with the first-principles predictions, in order to better understand the fundamental mechanical behavior of iridium.

9:20 AM

Influence of Trace Impurities on the High-Temperature Mechanical Properties of Iridium: B. Fischer[1]; *Andreas Behrends*[1]; D. Lupton[2]; J. Merker[2]; [1]Fachhochschule Jena, Univ. of Appl. Sci., Tatzendpromenade 1b, Jena 07745 Germany; [2]W. C. Heraeus GmbH & Company KG, Matls. Tech. Div., Heraeusstrasse 12-14, Hanau 63450 Germany

Iridium is used as a high temperature material at temperatures up to 2000°C, for example, for high-strength components in space technology. Trace impurities can favour the formation of intercrystalline cracks (processing problems) and reduce the necessary strength and ductility of iridium for this extreme field of application. Because no detailed data on the influence of trace impurities have been published, examinations were first carried out on the doping effect of the elements iron and silicon on high-purity iridium in different concentrations (27-1300 ppm). By means of a suitable production process, it is possible to avoid grain boundary segregations of trace elements which are difficult to remove under industrial conditions. The metal is now easier to process, the tendency to intercrystalline cracking is reduced and a larger amount of trace impurities is tolerable than was previously assumed. Only a small effect of the added elements on the stress-rupture strength of iridium at 2200°C in the short time range (<10 hours) could be observed. However, distinct differences in the creep behaviour of the doped heats were found relative to pure iridium.

9:40 AM

Brittle Transcrystalline Fracture in Plastic Face Centered Cubic Metal Iridium: *P. Panfilov*[1]; [1]Urals State University, Lab. of Strength, Ekaterinburg 62001 Russia

The main puzzle of iridium is an inclination to cleavage after severe plastic deformation. Evolution of transcrystalline cracks in bulk crystals and thin foils of iridium is the subject for discussion in this paper. Tested crystals did not content dangerous non-metallic impurities and level of metallic contaminants was minimal what allows considering brittleness as inherent property of iridium. Bulk crystals failed after considerable elongation, however, necking did not appear in them. It was shown that octahedral slip gives the main contribution to plastic deformation, therefore, mechanical twinning or non-octahedral slip could not be a cause for cleavage. Sharp cracks appeared in strengthened material near power concentrators of stresses. Sometimes, plastic deformation accompanied crack growth, but this did not lead to crack tip blunting. Motion of cracks on primary ({100}) and secondary ({210}) cleavage planes were observed. Evolution of cracks in thin foils was considered in detail. It is unbelievable, but cracking of iridium foils looks like fracture of ductile metal: microcracks emit both twins and perfect dislocation, dislocation emission causes crack tip blunting, and dangerous cracks possess zigzag profiles. In contrast with usual f.c.c.-metal, iridium foils contain high dense <110> dislocation nets, which bother emitted dislocation to move from crack tip, and, as a result, crack leaves ability to emit dislocations. After that crack should either stop or continue its growth without dislocation emission like crack in brittle crystal. Microcrack will have an opportunity to transform in zigzag crack if dislocation nets are absent around it. Observations of cracks have shown that brittle transcrystalline fracture is property of bulk iridium crystals only. TEM study allows revealing microscopic cause of brittleness in iridium, while its thin foils failed by ductile manner. This is its ability to store high dense dislocation nets. During preliminary deformation, plastic iridium crystal exhausts the resource of plasticity (nets cover all volume of crystal) and further loading should induce brittle fracture of sample.

10:00 AM Break

10:10 AM

Strength Behavior of Ir-Based Refractory Superalloys: *Y. Yamabe-Mitarai*[1]; *Y. Gu*[1]; Y. Ro[1]; S. Nakazawa[1]; T. Maruko[2]; H. Harada[1]; [1]National Institute for Metals, HTM21Project, 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047 Japan; [2]Furuya Metal Company Limited, No.1915, Morizoeshima, Shimodate, Ibaraki 308-0861 Japan

We have proposed "refractory superalloys" using platinum group metals, especially Ir, as ultra-high temperature materials. The refractory superalloys are defined as the alloys with an fcc and L12 two-phase coherent structure and with yet higher melting temperature than

Ni-based superalloys that are used as high temperature materials like turbine blade. High strength of Ni-based superalloys at high temperature is attributed to the fcc and L12 two-phase coherent structure. Compression strength, creep properties, and microstructure up to 1800°C were investigated in the Ir-V, Ir-Ti, Ir-Nb, Ir-Ta, Ir-Hf, and Ir-Zr binary systems. The fcc and L12 two-phase coherent structure formed in these alloys after heat treatment. The strengths of the two-phase alloys are higher than those of fcc or L12 single-phase alloys. This shows that the main factor contributing to strengthening is precipitation hardening. Precipitate shape depends on lattice misfit between the matrix and the precipitates. Plate-like and cuboidal precipitates formed in the alloys with large (2%) and small (0.3%) lattice misfit, respectively. Precipitation hardening is more effective for plate-like precipitates because shearing or bypass of dislocation is difficult for plate-like precipitates and coherency strain at the interface between matrix and precipitates is high by large lattice misfit. Deformation mechanism is discussed by observation of dislocation structures of deformed samples.

10:30 AM

Effect of Ir Addition on High-Temperature Strength of NiAl Single Crystals: *A. Chiba*[1]; T. Ono[1]; X. G. Li[1]; S. Hanada[2]; T. Sugawara[2]; [1]Iwate University, Dept. of Matls. Sci. and Tech., Morioka 020-8551 Japan; [2]Tohoku University, Instit. for Matls. Rsch., Sendai 980-77 Japan

In order to obtain the knowledge on mechanisms of enhancement of high-temperature strength of NiAl by Ir addition, compression and creep tests of soft [-223] oriented single crystalline NiAl and Ir-doped NiAl (Ni0.9Ir0.01Al) have been conducted in the temperature range from room temperature to 1473 K. CRSSs of Ni0.9Ir0.1Al single crystal are about a factor of 3, 4, and 6 higher than those of binary NiAl single crystal at room temperature, 1073 K and 1473 K, respectively. The Ni0.9Ir0.1Al single crystal deforms by kinking instead of slip of b=(-110)[001] dislocation which normally glide in binary NiAl single crystal with soft [-223] crystal axis. Secondary creep rate of Ni0.9Ir0.1Al single crystal is about a magnitude of 4 lower than that of binary NiAl single crystal at 1273 K; stress exponent of secondary creep for Ni0.9Ir0.1Al and NiAl is approximately 3.0 and 4.8, respectively. Dislocation substructures of crept Ni0.9Ir0.1Al single crystal consist of subboundaries and gliding dislocations, indicating that dislocations of Ni0.9Ir0.1Al single crystal are more difficult to move than those of binary NiAl single crystal. It is likely that addition of Ir to NiAl enhances the Peierls stress of (-110)[001] slip system of NiAl and leads to the activation of non-b=(-110)[001] dislocation and (or) kinking.

10:50 AM

Microstructure and Mechanical Properties of Quaternary Ir-Nb-Ni-Al Alloys: *X. Yu*[1]; Y. Yamabe-Mitarai[1]; T. Yokokawa[1]; M. Osawa[1]; Y. Ro[1]; H. Harada[1]; [1]National Research Institute for Metals, High Temp. Matls. 21 Project, 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047 Japan

Many attempts have been made in order to improve the temperature capability of Ni-based superalloys by adding more refractory elements into them, such as Re, W, Mo, Ta, et al. Single crystal Ni-based superalloys are classified by the level of Re content. But the biggest problem is phase stability. Since Re has a low diffusivity and tends to be segregated in matrix, the addition of Re assists in the formation of a topologically close-packed (TCP) phase. Another question is the melting temperature of Ni (1450°C). It can not be used at higher temperature. Developing new alloys whose matrix elements are of higher melting temperature is another way. Ir attracts researcher's attention due to the higher melting temperature (2240°C) and superior oxidation and the fcc/L12 coherent structure in Ir-based alloys. The fcc/L12 coherent structure provides a challenge for combining Ir- and Ni-based alloys to prepare new alloys. Therefore, we do the efforts to investigate quaternary Ir-Nb-Ni-Al in the last two years. The previous results indicated the two kinds of fcc/L12 (fcc/Ir_3Nb and fcc/Ni_3Al) coherent structure formed in some alloys and strength also increased drastically compared to Ni-based superalloys. These alloys are promising to be used at higher temperature. However, the microstructure evolution of quaternary Ir-Nb-Ni-Al alloys is not clear, element distribution and lattice misfit of two kinds of fcc/L12 in the same quaternary Ir-Nb-Ni-Al alloys have never been studied. Therefore, in the present paper, microstructure evolution, element distribution and lattice misfit of two kinds of fcc/L12 as well as 0.2% flow stress at room temperature and 1200°C in quaternary Ir-Nb-Ni-Al will be investigated.

11:10 AM

The Effects of Nb Content and Third Element Additions on the Fracture Behaviours of Polycrystalline Ir-Nb Two-Phase Alloys: *Y. Gu*[1]; *Y. Yamabe-Mitarai*[1]; *H. Harada*[1]; [1]National Research Institute for Metals, HTM 21 Project, 1-2-1 Sengen, Tsukuba, Ibarake 305-0047 Japan

Iridium (Ir) and its single-phase alloys have been tried as structural materials for ultra-high temperature applications, such as solar thrusters in lightweight solar concentrators for use in space and as postimpact containment claddings for radioactive fuel. Ir and its alloys were chosen for these applications because of their high melting point, excellent oxidation resistance, and welding suitability. However, polycrystalline Ir and its alloys normally exhibit grain-boundary (GB) fracture with limited ductility in tensile tests at temperatures below 800°C. Moreover, alloys with single-phase normally show less resistant to creep deformation, a property that is important for structure materials at high temperatures. Recently, we developed a new class of two-phase superalloys, namely, refractory superalloy, based on platinum group metals (PGMs). These refractory superalloys have a coherent fcc-L12 structure, similar to γ/γ' microstructure in nickel-base superalloys, and have good potentiality as structural materials used at ultra-high temperatures up to 2000°C. Preliminary results showed that, of these refractory superalloys, Ir-based fcc-L12 two-phase alloys, such as Ir-15 at % Nb, Ir-15 at % Hf, and Ir-15 at % Zr alloys, were superior in high temperature strength and oxidation resistance. Despite the importance of the relationship between the microstructures and deformation behaviours of these refractory superalloys for practical applications, the fracture behaviour was also needed to be understood. The aims of the present study are: (i) to examine the effects of various niobium (Nb) contents on the microstructures and fracture behaviours of Ir-Nb two-phase refractory superalloys, (ii) to identify third element (Ni, Mo, C, and B) addition on the microstructures and fracture behaviours of Ir-15 at % Nb alloy, and (iii) to determine the relationship between the microstructure and fracture behaviour of the alloy. Our results showed that the intergranular fracture occurred in Ir single-phase alloys could be governed by controlling the microstructures around grain-boundary (GB) and alloyed with some third elements.

11:30 AM

Mechanical Behavior of Ir-Sn Layered Crystals: *P. Panfilov*[1]; Y. L. Gagarin[1]; A. V. Yermakov[2]; [1]Urals State University, Lab. of Strength, Ekaterinburg 62001 Russia; [2]Ekaterinburg Non-Ferrous Metals Processing Plant, The Head of Rsch. Ctr., Lenin Ave. 8, Ekaterinburg 620014 Russia

Iridium based compounds are prospective materials for exploitation in aggressive environments, but poor plasticity and brittleness make considerable doubts for their industrial applications. Elaboration of layered iridium compounds would help to solve the problem of technological brittleness, in as much as layered structure of sample could suppress crack growth and provide plastic deformation even in brittle crystals. Single crystals of Ir-Sn compound were grown by means of high temperature synthesis in vacuum. Silver lustrous and metallic electric conductivity was inherent to crystals. Chemical analysis has shown that material contains Ir and Sn in proportion of 1:1. Samples possessed tetragonal lattice with ratio of c/a<<1 and their morphology was similar to "sandwich" formed from one hundred thin square plates (thickness of each plate is 10^{-3}mm). These features did not allow to built simple crystallographic model for the compound. Samples were indented by Vickers diamond pyramid at room temperature. Deep holes remained on the surface after indentation, but this did not lead to the separation of crystal. Sliding of plates or single crystal layers is the main mechanism, which provides severe plastic deformation in vicinity of indents. Twin lamellas in <110> direction and cracks along <100> and <110> were observed in deformed single crystal layer. Cracks have only appeared near indents, while twins were detected on the whole crystal. It was revealed that cracks in the first layer could not pass in depth of crystal.

Kleppa Symposium on High Temperature Thermochemistry of Materials: Session I

Sponsored by: ASM International: Materials Science Critical Technology Sector, Extraction & Processing Division, Thermodynamics & Phase Equilibria Committee, Process Fundamentals Committee

Program Organizers: Ray Y. Lin, University of Cincinnati, Department of Materials Science and Engineering, Cincinnati, OH 45221-0012 USA; Y. Austin Chang, University of Wisconsin, Department of Materials Science & Engineering, Madison, WI 53706-1595 USA; Dr. Susan Meschel, The University of Chicago, Chicago, IL 60637 USA; Ramana Reddy, University of Alabama, Department of Metals and Materials Engineering, Tuscaloosa, AL 35487 USA

Monday AM — Room: Lincoln E
March 13, 2000 — Location: Opryland Convention Center

Session Chairs: Susan V. Meschel, University of Chicago, Chicago, IL 60637 USA; J. C. Gachon, Universite Henri Poincare, Lab de Chimie du Solide Mineral, Vandoeuvre, Cedex 54506 France

8:30 AM

Some Like it Hot: Evolution and Applications of High-Temperature Reaction Calorimetry at University of Chicago from 1952 to 2000: *Ole J. Kleppa*[1]; [1]University of Chicago, James Franck Instit., Chicago, IL 60637 USA

The author will present a review of his work in the field of high-temperature reaction calorimetry. This review will be partly historical, partly scientific. He will touch on his work on low-melting liquid alloys, on the thermochemistry of some Hume-Rothery type binary alloys, on the heats of mixing of molten salts, on the development of oxide melt solution calorimetry, on the thermodynamics and thermochemistry of metal-hydrogen systems, and on the development and construction of a number of different reaction calorimeters suitable for work at temperatures up to about 1200°C. Finally he will give an introduction to his more recent investigations of refractory intermetallic and related compounds. This section will include an outline of the special technique of solute-solvent drop calorimetry, a technique which is particularly suitable for very refractory compounds. However, most recently his studies of refractory compounds have emphasized the thermochemistry of congruent melting compounds with melting points below about 2000°C using direct synthesis calorimetry at 1200°C. More detailed discussions of these investigations will be presented in the invited papers given by his co-workers S. V. Meschel and Qiti Guo.

9:15 AM

Contributions to Molten Salt Chemistry by Ole J. Kleppa: *Milton Blander*[1]; [1]Quest Research, 1004 E. 167th pl., South Holland, IL 60473-3114 USA

Ole Kleppa and associates have accurately measured the enthalpies of mixing of a large number of binary molten salt systems. These results have also been proven to be useful in the analyses of phase diagrams and in creating a reliable database on free energies of mixing of a large number of systems. He made a general confirmation of a specific result by Hildbrand and Salstrom that excess free energies of mixing of simple binary molten salts could be represented by a simple polynomial, an important result for ionic systems with very long range ionic pair interactions. His measurements of the enthalpies of mixing of all binary alkali nitrates led to an expression which was close to that deduced form a simple model by Forland. This result also catalyzed the Conformal Ionic Solution Theory, the only theory fundamentally valid for molten salts. This theory later led to methods for accurately predicting the solution properties of multicomponent molten salt systems from data on the subsidiary binaries and the pure component salts. His measurements of binary systems with the two components having the same cation and two different anions indicated that deviations from ideality were generally very small. A theoretical extension of this conclusion to silicates and other polymeric slags led to reliable predictions of the solubilities (and sulfide capacities) of ionic compounds. Kleppa's work has had a major influence on molten salt and slag chemistry.

9:45 AM

Thermochemical Studies of Oxynitrides by Oxidative High Temperature Solution Calorimetry: *Alexandra Navrotsky*[1]; [1]University of California, Dept. of Chem. Eng. and Matls. Sci., Thermochem. Facility, Davis, CA 95616 USA

Thermodynamic properties of nitrides and oxynitrides are poorly known, despite technological importance and scientific interest. Recent advances in oxidative drop solution calorimetry of nitrogen-containing materials in molten oxide solvents at 973-1073 K enable the determination of enthalpies of formation. The calorimetric methodology is described and applied to three groups of materials: the beta sialons in the Si-Al-O-N system, cubic oxynitrides in the Zr-O-N and Zr-M-O-N(M = Y, Ca, Mg) systems, and phosphorus oxynitrides in the P-O-N and Li-P-O-N systems. The energetics of oxygen-nitrogen substitution these systems is discussed in terms of crystal chemistry, bond strengths, and short range order.

10:15 AM Break

10:30 AM

What Will Be Done in the Future with the Enthalpy Data Set of O. J. Kleppa: *Jean Hertz*[1]; [1]Universite Henri Poincare-Nancy I, Lab. de Thermodyn. Metallu., Umr Cnrs 7555, Chimie du Solide Mineral BP 239, Vandoeuvre, les Nancy-Cedex 54506 France

After 40 years or more of experimental work devoted to thermochemistry of metallic alloys it will be time to wonder: what will be done in the future, by the scientific community, with the patrimony of data I have obtained? This question is of particular importance for O. J. Kleppa with his fantastic panel of consistent enthalpy data, obtained by his group for more than 45 years of unbroken calorimetry experiments relative to more than 200 different binary systems. The progress of phase diagram calculation of multicomponent systems, is significant as far as industrial applications for new alloys development and metallurgical processes are now in due course. That will be the main topic of the near future metallic thermodynamics. That means that very simple models are generalised: the Redlich-Kister multicomponent model, coming from the petroleum industry, and the Hillert sublattice model for intermediate phases provide a very large domain of applications, useful for the main multicomponent metallic systems. Unfortunately such works cannot start out of nothing, but out of consistent thermodynamic data used to fit the binary systems first, then the ternaries. Higher order terms are generally not needed. The enthalpy of mixing of the liquid phase in the whole range of composition and the enthalpy of formation of compounds are of significant interest to obtain a set of coherent multicomponent data bank. In the 80[ies] we have trusted the progress of band theory and physical quantum mechanics to provide a lot of "ab initio" or semi-fitted energetic data set. Unfortunately the relative phase stability in a multicomponent system depends on only some hundredth of eV and the precision of the calculated cohesive energy will not attain 0.1 eV in the more accurate results. The interest of this part of the physical thermochemistry remains for understanding the metallic bonding, but not for practical applications. In my opinion and for a very long period the only source of information for realistic metallic multicomponent phase diagram previsions will be the good experimental binary and ternary data: enthalpy and chemical potential measurements, each one needed to calibrate the two enthalpy and entropy contributions of the Gibbs-function. Experimental equilibrium lines and tie-lines in phase diagrams could be considered as equivalent to a Gibbs-function information, when calorimetric data are available. For this reason the large Kleppa enthalpy data set patrimony will be of crucial interest for a

very long future period. We will illustrate this prognosis with various multicomponent diagram previsions in the field of low melting metals.

11:00 AM

Excess Thermodynamic Functions of Systems with N (N>6) Components: Measurements and Calculations: *M. Gambino*[1]; J. P. Bros[1]; Z. Moser[2]; M. Hoch[3]; [1]Universite de Provence, Iusti, Ura-Cnrs 6995, Rue Enrico Fermi 5, Marseille, Cedex 13 13453 France; [2]Instytut Podstaw Metallurgii im., Alexandra Krupkowskiego Pan, Krakow, ul Reymonta 25 30-059 Poland; [3]University of Cincinnati, Dept. of Matls. Sci. and Eng., Cincinnati, OH 45221-0012 USA

We measure the enthalpy of mixing along a line connecting the center of the system with one component, and the partial enthalpy at the center of the system for all components. The calorimeter is a high temperature Calvet type calorimeter, operating between 700 and 1000 K. For the calculations we use the Hoch-Arpshofen model, which uses only binary interactions. The agreement between calculated and measured data is better than ±5%. Thus only a relatively few measurements are needed to understand the complete system. We discuss here the 7 component system (Bi-Cd-Ga-In-Pb-Sn-Zn). Measurements and calculations of Zn activity in the system (Bi-Cd-Pb-Sn-Zn) show similar excellent agreements.

11:30 AM

Thermochemistry of Alloys of Transition Metals and Lanthanide Metals with Some IIIB and IVB Elements in the Periodic Table-An Overview: *S. V. Meschel*[1]; O. J. Kleppa[1]; [1]The University of Chicago, James Franck Instit., 5640 S. Ellis Ave., Chicago, IL 60637 USA

We have in this laboratory conducted systematic studies of the thermochemistry of transition metal and rare earth alloys by high temperature calorimetric methods. An overview of the thermochemistry of the alloys of the transition metals and lanthanide metals with elements in the IIIB and IVB columns of the periodic table will be presented. The enthalpies of formation of most of these compounds were determined by high temperature direct synthesis calorimetry. This review will summarize the trends between the enthalpies of formation of the TR-X and LA-X alloys (where X is a IIIB or IVB element) and the atomic numbers in each transition metal and lanthanide metal family. We will compare our measured enthalpies of formation of each alloy family for the 3d, 4d and 5d transition metal elements. We will also compare our experimental measurements with predicted values on the basis of Miedema's semi-empirical model. This review will show examples of a correlation between the enthalpies of formation of the alloys of the lanthanide elements with the non-metal elements in the IIIB and IVB columns in the periodic table. We will also show some comparisons of our measured enthalpies of formation with the predictions by Gschneidner for the lanthanide alloys.

12:00 PM

Abstract Text Is Unavailable: *F. Sommer*

Light Metals Division Plenary Session: Aluminum Plenary

Sponsored by: Light Metals Division, Aluminum Committee
Program Organizer: Ray D. Peterson, IMCO Recycling Inc., Rockwood, TN 37854 USA

Monday AM — Room: Presidential Ballroom
March 13, 2000 — Location: Opryland Convention Center

Session Chair: Ray D. Peterson, IMCO Recycling Inc., Rockwood, TN 37854 USA

8:00 AM Introductory Remarks
Dr. Ray Peterson, IMCO Recycling Inc., Rockwood, TN 37854 USA

8:10 AM

An Overview of the Aluminum Industry: *Richard B. Evans*[1]; [1]President, Alcan Global Fabricatin Group, 6060 Parkland Blvd., Cleveland, OH USA

An overview and outlook of the global aluminum industry will be presented. A focused look on aluminum's two largest markets, packaging and transportation, will be given.

8:40 AM

Materials Used in Aluminium Smelting: *Harald A. Oye*[1]; [1]Norwegian University of Science and Technology, Instit. of Chem., Trondheim N-7491 Norway

The production of alumina, anode and cathode carbon will be reviewed from a historic and the present point of view. Problems, challenges and new future advances will be discussed.

9:10 AM

Advancing the Hall Heroult Electrolytic Process: *Barry Welch*[1]; [1]The University of Auckland, Dept. of Chem. and Matls. Eng., Private Bag, Auckland 92019 New Zealand

The design and operating advances achieved in the last quarter century will ensure the Hall Heroult technology will maintain a competitive advantage over alternative aluminium production processes for some time into the future. The advances were lead by magnetic compensation and computerised process control coupled with electrolyte optimization. These enable larger more economic cells to be designed. During the same time the fundamental studies have enabled a better understanding of the subtleties of the processes and secondary reactions that were ignored in the theoretical understanding whilst the cells performed poorly. These secondary processes, including reactions associated with impurities and anodes consumption, those leading to onset of anode effect, and alumina dissolution kinetic have not been fully exploited yet. Today as the focus shifts to higher productivity, the dynamics of the cell and the impact operations have on the very finely tuned heat balance becomes more important. With the high current efficiencies and low margins for error in modern cells the present challenge is to refine designs, control strategy and operating practices so that further marginal gains and economic performance can be achieved. This will include better management of aluminium fluoride, prevention of anode effects, and earlier detection of the increasingly prevalent anode spikes. Super structure design changes coupled with improved control and practice will also enhance productivity of future generations of cells.

9:40 AM Break

10:00 AM

A Perspective on Aluminum Melting and Metal Treatment: *C. Edward Eckert*[1]; [1]Apogee Technology Inc., 1600 Hulton Rd., P.O. Box 101, Verona, PA 15147-2314 USA

Essentially all commercially significant aluminum produced shares a common processing history; melting and metal treatment. These two operations therefore have a monumental impact on production costs, the ultimate quality of end-use products, and also have an ancillary influence on environmental issues. Melting and metal treatment processes understandably remain developmentally topical. The technological heritage of aluminum melting and metal treatment will be chronicled, and, importantly, significant technical milestones identified. These milestones are associated with specific product/commercial imperatives or a revolutionary development. An example of the former is the emergence of the aluminum beverage container in the 1960 timeframe, while the latter is exemplified by rotary impeller in-line treatment. Finally, an inventory will be provided of contemporary aluminum melting and metal treatment technology, critical needs assessed, and a projection offered of future development.

10:30 AM

Aluminum Solidification Processing-Prospective and Retrospective Views of the Industry and the Field: *Diran Apelian*[1]; [1]Worcester Polytechnic Institute, Aluminum Cast. Rsch. Lab., Met. Proc. Instit., Worcester, MA 01609 USA

During the last 50 years, aluminum has evolved into one of the most important societal materials; it is used in a variety of diverse

applications-construction, automotive, aerospace, packaging, furniture, jewelry and a vast number of products, which once were made from ferrous or other materials. Specifically, during the last decade, we have seen significant increases in the use of cast aluminum net-shaped manufactured components. For example, in 1980 there were 800,000 tons of aluminum casting shipments in North America versus 1,800,000 tons in 1998. In this plenary lecture, a prospective review of the science and technology of aluminum metalcasting will be presented, for both primary aluminum production as well as metalcasting. This will be followed with a retrospective presentation of the emerging technologies and challenges we face. The plenary lecture will be a holistic review of solidification processing of aluminum, addressing: where we have been, where we are going, and what are the exciting frontiers facing the industry.

11:00 AM

Aluminum Fabrication and Applications: *Elwin L. Rooy*[1]; [1]Elwin L. Rooy and Associates, 461 Ravine Dr., Aurora, OH 44202 USA

Modern manufacturing strategies combine solidification and thermomechanical process technologies for optimum efficiency, product quality and reliability, and product performance. The present and future importance of incorporating melt processing and solidification considerations into the sequence of down-stream operations for satisfying product requirements and for developing new competitive market capabilities forms an essential basis for these strategies. The majority of aluminum is consumed in fabricated forms ranging from rolled products to components formed by powder metallurgy. Remelted and cast products represent a rapidly growing manufacturing sector. The evolution of processes for aluminum's multivaried commercial shapes and forms paralleled the industry's success in determined applications and market penetration. The history of the aluminum industry's development of casting, forging, extrusion and rolled products and the significance of process and product developments to the dramatic evolution of aluminum as the metal of the twentieth century is reviewed, and current and projected developments are outlined.

Magnesium Technology 2000: Electrolytic Technology

Sponsored by: Light Metals Division, Reactive Metals Committee, International Magnesium Association
Program Organizers: Howard I. Kaplan, Magnesium Corporation of America, Salt Lake City, UT 84116 USA; John N. Hryn, Argonne National Laboratory, Argonne, IL 60439-4815 USA; Byron B. Clow, International Magnesium Association, McLean, VA 22101 USA

Monday AM — Room: Bayou C
March 13, 2000 — Location: Opryland Convention Center

Session Chair: Ramaswami Neelameggham, Magnesium Corporation of America, Salt Lake City, UT 84116 USA

8:30 AM Invited, Keynote

Magnesium Industry Growth in the 1990 Period: *Robert E. Brown*[1]; [1]Magnesium Monthly Review, 226 Deer Trace Rd., Prattville, AL 36067-3806 USA

The world magnesium industry has experienced a continuing growth of 6 per cent or more per year for over 10 years. Major growth has been in the die casting sector which has grown as much as 14% per year over the last 10 years. New magnesium projects are being announced frequently. In many countries there are large magnesium projects being discussed, studied, designed and constructed. Unfortunately, there is much more discussion than there is construction. A review of the total magnesium supply situation shows a great paradox. The prices of magnesium will have to be lowered to successfully market all of the magnesium production tonnage that is being discussed. Lowered prices makes the economics of a new magnesium plant much less favorable. One of the big problems is process technology. There are literally no processes commercially available that have demonstrated sufficient development to be able to produce magnesium metal economically. The closest technology is the Alcan cell, but it requires a very dry and pure anhydrous magnesium chloride feed. This is the basic area where every project past, present and future has had problems. These problems are still not solved in as this paper is being written.

8:55 AM

Magnesium Electrolysis-A Monopolar Viewpoint: Oddmund Wallevik[2]; *Ketil Amundsen*[1]; André Faucher[3]; Thorvald Mellerud[4]; [1]Hydro Magnesium, Oslo N-0246 Norway; [2]Norsk Hydro ASA, Rsch. Ctr., Porsgrunn N-3901 Norway; [3]Norsk Hydro Canada, Bécancour, Canada; [4]Hydro Magnesium, Brussels, Belgium

Norsk Hydro has produced magnesium in Porsgrunn, Norway, since 1951. The technology including the electrolysis was "inherited" from IG Farben. Hydro has since then continuously developed the magnesium electrolysis, first by improving the IG technology, and then by developing its own "diaphragmless electrolyser" (DLE), now being used for a number of years in Norsk Hydro's plants in Porsgrunn as well as in Bécancour, Québec. A presentation will be made of the Norsk Hydro high-amperage monopolar electrolysis cell. Its performance will be described, as a basis for the conclusion that this type of cell presently is very competitive compared to bipolar cell technologies, although it has a higher energy consumption.

9:20 AM

Investigation on Electrocatalysis for Energy Saving in Magnesium Electrolysis: *Zhong Xie*[1]; Ye-Xiang Liu[1]; [1]Central South University of Technology, Dept. of Nonfer. Metallu., #2 Lushan Nan Rd., Changsha, Hunan 410083 PRC

In the present paper, we report some research results on electrocatalysis for chlorine evolution reaction (CER) in Mg electrolysis. Investigation has been carried out on various oxide electrodes in equimolar NaCl-KCl melts at 700°C. Oxide electrodes were prepared by thermal decomposition procedure on graphite substate. Steady state linear potential sweep and an improved current interruption technique were used to investigate the electrocatalytic activity of transition metal oxides, rare earth oxides and their mixed oxides. Pr6O11, Tb4O7, Tm2O3, RE+Ru and CoxFeyOz (x=0.75,y=2.25,z=4) mixed oxides showed good active for CER, reducing anode overpotential up to 80-110 mv at a current density of 0.6A/cm.sq. compared with graphite electrode. 200-250kWh/T-Mg energy saving could be achieved if above mentioned electrodes being employed in Mg electrolysis. Attempt was made to elucidate the electrocatalysis mechanism.

9:45 AM

Inert Anodes for Magnesium Electrolysis: Jerry F. Moore[1]; *John N. Hryn*[1]; Michael J. Pellin[1]; W. F. Calaway[1]; Kevin Watson[2]; [1]Argonne National Laboratory, Energy Sys. Div., 9700 S. Cass Ave., Argonne, IL 60439 USA; [2]Noranda Inc., Noranda Tech. Ctr., 240 Boul. Hymus, Pointe-Claire, Quebec H9R1G5 Canada

Magnola Metallurgy Inc. (MMI) will commission a 63,000 tpa primary magnesium production plant in June 2000. The plant will produce magnesium using electrolysis cells with industry standard carbon anodes. Undesirable by-products of the electrolysis process with carbon anodes are chlorinated hydrocarbons (CHCs). These represent a significant environmental concern, which MMI are committed to reducing and eventually eliminating. One possible means to prevent the production of CHCs is to replace the carbon anodes with non-carbon "inert" anodes. The development of a viable inert anode material has been a goal for the magnesium industry for many years. To date, no acceptable material has been found. The major technical hurdle is to develop a material with the ability to withstand chlorination by the evolving chorine gas on the anode surface whilst conducting electrical current efficiently. Argonne National Laboratory (ANL) has identified certain metal alloys that are promising candidate materials for inert anodes. These alloys form self-limiting surface oxide films that are thin enough to allow current to pass, yet thick enough to prevent chlorination of the underlying metal. ANL are investigating the use of these alloys as inert anodes under the joint sponsorship of MMI and the U.S. DOE, Office of Science, Laboratory Technology Research

Program. This paper presents a review of previous inert anode research and an update of the ANL project.

10:10 AM Break

10:20 AM

The Magnola Demonstration Plant: A Valuable Investment in Technology Development and Improvement: *K. Watson*[1]; P. Ficara[2]; M. Charron[2]; J. Peacey[2]; J. Primak[2]; [1]Noranda Inc., Noranda Tech. Ctr., Pointe-Claire, Quebec Canada; [2]Magnola Metallurgy Inc., Magnola Proj. Off., 620 Rene-Levesque W., 10th Fl., Montreal, Quebec H3B1N7 Canada

Noranda will become a major producer of magnesium following the commissioning of its 63,000 tpa Magnola plant in June 2000. The Magnola plant will utilise new process technology to extract magnesium from serpentine mine tailings. The technology is unique and will enable Noranda to become the world's premier primary magnesium producer. This paper presents an historical overview of the Magnola project from the preliminary process development at Noranda Incorporated's Technology Centre through to operation of the pilot demonstration plant in 1996 & 1997 and finally to design of the full scale Magnola plant. In particular, this paper will present some of the major conclusions and improvements derived from the demonstration plant stage and will evaluate their impact on the development of the overall Magnola Process. An update of the current status of the plant construction and pre-commissioning is also provided.

10:45 AM

Magnesium Electrolytic Production Process: G. Shekhovstov[1]; V. Shchegolev[1]; *V. Devyatkin*[1]; V. Tatakin[1]; I. Zabelin[1]; [1]Titanium Institute, 180 Prospect Lenina, Zaporozhue 330035 Ukraine

The Titanium Institute/VAMI proposes two variants of the magnesium electrolytic production process. The first variant is based on a two-stage preparation process of magnesium raw material carnallite (KCl.MgCl2.6H2O) for electrolysis. In the first stage, carnallite is dehydrated in fluidized bed dryers with output of 400 t/day. Operation and control of the drying process is highly automated. The second stage of carnallite dehydration is carried out in electric chlorinators with output of 150-200 t/day. In the chlorinators, carnallite is melted and chlorine treated. Molten carnallite flows to the electrolysis cells. The electrolysis cells are connected in a flow line that operates as one highly productive electrochemical unit. By electrolyte flow, magnesium moves through the electrolysis cells and is accumulated in a separator cell where it is extracted and passed to the casting house for casting magnesium and magnesium alloys into ingots. Electrolysis cells current is about 200-300 kA. Magnesium and magnesium alloys are refined in continuous refining furnaces with the capacity of up to 100 t/day. The process is adopted by magnesium and titanium-magnesium plants of Russia, Kazakhstan, and Ukraine. The best modern projects are realized at the DSM magnesium plant in Israel. The second variation of magnesium electrolysis production process is based on carrying out high dehydration of carnallite in fluidized bed dryers by HCl injection into chambers together with combustion gases. HCl is gained from fuel burning in chlorine gas in magnesium electrolysis cells. Solid highly dehydrated carnallite is charged into cells connected into flow lines having centralized magnesium collection. This process has passed pilot-commercial tests and is ready for industrial realization. The above-mentioned carnallite processing variants can be used for different types of raw material: magnesite, chlorine-magnesium solutions, sea water, dolomite, and carnallite.

11:10 AM

Solid-Oxide Oxygen-Ion-Conducting Membrane (SOM) Technology for Direct Reduction of Magnesium from Its Oxide: *D. E. Woolley*[1]; U. B. Pal[2]; G. B. Kenney[3]; [1]Boston University, Boston, MA USA

Abstract Text Not Available

11:35 AM

Comparison of Fused Cast Alumina Products for Magnesium Chloride Cells: *Alexandre Mauries*[1]; D. A. Whitworth[1]; [1]SEPR, R&D, B.P. #1, Le Pontet, Cedex 84131 France

The molten salt electrolysis of magnesium chloride requires high quality refractories. The reduction of silicon dioxide by magnesium involves the use of high alumina refractories. The sintered refractories fail because of the penetration of the low viscosity salts into the open porosity. The high alumina fused cast refractories appear to be the best solution in this application. Different types of high alumina fused cast products have been prepared and tested in SEPR laboratory. The main properties demanded by the application have been taken into account: low penetration by the molten salts (porosity, cracks, crystal size), chemical stability in contact with MgCl2, high electrical resistivity. Some general trends can be drawn regarding the application of fused cast alumina products in magnesium chloride cells.

Opportunities for Materials & Engineering Research Funding From Government & Industry: Session 1

Sponsored by: TMS, Public & Governmental Affairs Committee, Young Leaders Committee

Program Organizers: Canan U. Hardwicke, General Electric Company, GECRD, Niskayuna, NY 12309 USA; Samuel A. Davis, TIMET, Henderson, NV 89009 USA

Monday AM — Room: Bayou A
March 13, 2000 — Location: Opryland Convention Center

Session Chairs: Canan U. Hardwicke, General Electric Company, GECRD, Niskayuna, NY 12309 USA; Samuel A. Davis, TIMET, Henderson, NV 89009 USA

8:30 AM

An Outline of the Federation of Materials Societies (FMS): *John N. Mundy*[1]; [1]Consultant, 10720 Game Preserve Rd., Gaithersburg, MD 20879-3106 USA

FMS is an umbrella organization whose member societies and affiliates represent the professional societies, universities and National Research Council Organizations which are involved with materials science, engineering, and technology. The purpose of FMS is to aid the materials community in obtaining information from and exchanging information with the policy community. An important FMS goal is to help the materials community to arrive at consensus materials policy and to assist it in informing policy makers of materials concerns. TMS is a contributing member of FMS and it is valuable for members of TMS to be aware of how FMS fulfills these tasks.

8:55 AM

An Overview of R&D in the Federal Government with Emphasis on DOE's Materials Research Programs: *Louis Ianniello*[1]; [1]DOE (retired)

Research funding by the Federal Government approximates $80 billion per year, covering basic, applied and technology development, both defense and civilian areas. Materials research is conducted and supported to some extent by almost every agency of the government. The three largest Materials Research funding agencies for external support are the Department of Defense (DOD), the National Science Foundation (NSF), and the Department of Energy (DOE). The talk will help the audience put the Materials Research portion of the Federal budget into perspective and then provide some detailed information on the DOE programs. DOE conducts research at its own laboratories and also funds research proposals submitted in response to solicitations as well as unsolicited proposals. The talk will include information on the various offices that fund materials research and on opportunities for doing research and interacting technically with different DOE programs.

9:20 AM

Materials Opportunities in Energy Efficiency: *Toni Grobstein Marechaux*[1]; [1]U.S. Department of Energy, EE-20, 1000 Independence Ave. S.W., Washington, DC 20585-0121 USA

Energy its production, use, and conservation is a huge part of the world economy, and materials enable much of the new technology needed to improve energy production and to use it more efficiently. The Office of Energy Efficiency and Renewable Energy in the US Department of Energy provides a wide variety of options in funding for research and development, from small grants for the development of inventions to industry cost-shared demonstration projects, and many types of research and development in between. Opportunities for materials funding in the areas of industrial, transportation, power, and building technologies will be discussed.

9:45 AM

Opportunities for Materials Technologies in the Advanced Technology Program: *Clare M. Allocca*[1]; [1]NIST, Adv. Tech. Pgm., 100 Bureau Dr. Stop 4730, Bldg. 101, Rm. A225, Gaithersburg, MD 20899-4730 USA

The NIST Advanced Technology Program (ATP) is a unique partnership between government and private industry to accelerate the development of high-risk technologies that promise significant commercial payoffs and widespread benefits for the economy. The Materials Technology community has already taken advantage of several ATP opportunities, and as a result has moved ahead. Following an overview, this presentation will describe past and potential accomplishments/opportunities in the area of materials technologies, including engineered surfaces and innovative forming techniques. In the area of engineered surfaces, industry has identified high risk, critical technical investments to include: (1) simultaneously improving engineered surface process designs and reducing cost through reduced development time and increased yield and consistency; and (2) developing extremely reliable and predictable surfaces which are integral to the design and operation of a component, as opposed to mere life enhancement. Tools (e.g., process diagnostics and life/performance prediction) and corresponding validation strategies have been identified as key to overcoming these barriers. In the area of innovative forming techniques, industry has identified, as appropriate for ATP, technical barriers to implementation of rapid prototyping/solid freeform fabrication, the aspects of metals (and metal matrix composites) forming which represent a major leap forward rather than an incremental step, and next generation technologies for ceramics and ceramic matrix composites forming. Potential investment areas include predictive tools for process control and scale-up, intelligent tool design, and innovative approaches to design optimization and automation.

10:10 AM Break

10:20 AM

Thoughts on Federal Research Funding in MSE with Specific Examples Related to the National Science Foundation: *Bruce A. MacDonald*[1]; [1]National Science Foundation, Div. of Matls. Rsch., 4201 Wilson Blvd., Rm. 1065, Arlington, VA 22230 USA

There are widespread opportunities for research support by the U.S. Federal Government in materials science and engineering. This can be viewed as an advantage since an investigator is not tied to one particular source for funding. The disadvantage is that there is no single key to gaining federal support since the various funding agencies may have different goals and funding criteria. Clearly the pursuers of funds should be aware of the objectives and proposal requirements of the agency from which they are requesting support. Gaining this knowledge is complicated by the fact that the funding environment is dynamic; therefore, it is incumbent upon the investigator to maintain frequent contact with the agencies from which they want and/or have support. In this discussion I will suggest ways in which this contact can be developed, as well as describing various research initiatives at the NSF.

10:45 AM

Collaborative Research Opportunity for New Faculty: *Reza Abbaschian*[1]; [1]University of Florida, Dept. of Matls. Sci. and Eng., Gainesville, FL 32611-6400 USA

Materials science and engineering research in U.S. universities has been sponsored mainly by the federal government. The mission oriented agencies (mainly DOD and DOE) have provided about 60% of academic research. The agencies, however, have been shifting funds toward applied and systems-oriented research. Many U.S. industries have also eliminated central research laboratories to align their R&D activities more closely with immediate business opportunities. Within academia, the pressure on the faculty remains the same, to educate as many graduate students as they can support. In light of the above, more research in universities is being conducted collaboratively, and in partnership with industry and government laboratories. This provides great opportunity for new faculty to establish their own graduate training and research programs. However, a proper balance between collaborative and individual research must be maintained.

11:10 AM

University/Industry Cooperative Applied Research Initiative: How It Works: *Manoranjan (Mano) Misra*[1]; [1]University of Nevada, Metallu. and Matls. Eng., Mackay School of Mines, Reno, NV 89557 USA

The thrust of this paper is to highlight the successful accomplishments of the Applied Research Initiative program at the University of Nevada, Reno. The industry/university partnership has brought several industries to work with junior and senior faculty in many research projects in the Metallurgical Engineering program. In addition, the program helped in generating large scale funding from the federal agencies. In this talk, several factors including how to develop such infrastructure will be discussed.

Packaging & Soldering Technologies for Electronic Interconnects: Soldering and Packaging Technologies

Sponsored by: Electronic, Magnetic & Photonic Materials Division, Electronic Packaging and Interconnection Materials Committee

Program Organizers: Hareesh Mavoori, Bell Laboratories, Murray Hill, NJ 07974 USA; Srini Chada, Motorola, Plantation, FL 33322 USA; Gautam Ghosh, Northwestern University, Department of Materials Science, Evanston, IL 60208-3108 USA; Martin Weiser, AlliedSignal Electronic Materials, Plated and Discrete Products, Spokane, WA USA

Monday AM — Room: Lincoln D
March 13, 2000 — Location: Opryland Convention Center

Session Chairs: G. Ghosh, Northwestern University, Dept. of Mats. Sci., Evanston, IL 60208-3108 USA; P. T. Vianco, Sandia National Laboratories, Matls. Joing Dept., Albuquerque, NM 87185-1411 NM USA

8:30 AM Opening Remarks

8:35 AM Invited

Solder Reaction on Electroless Ni(P) in Low Cost Flip Chip Technology: *K. N. Tu*[1]; [1]University of California, Dept. of Mat. Sci. Eng., Los Angeles, CA 90095-1595 USA

The wetting reaction between eutectic SnPb solder and electroless-Ni(P) under-bump-metallization has been studies by SEM, TEM, EDX and e-probe microanalysis. Two findings are interesting. The first is the enhanced crystallization of the electroless Ni(P), which has an amorphous structure in the as-plated state. The second is the lateral penetration of solder along the interface between the electroless Ni(P) and the dielectric SiON substrate. The crystallization leads to the formation of Ni_3P and Ni_3Sn_4 compounds. The penetration is accompanied by the formation of Ni_3Sn_4 compound. The kinetics of the crystallization and penetration will be presented.

8:55 AM Invited

Evolution of Interfacial Morphology during Reaction of Copper and Electroless Nickel with Eutectic Pb-Sn Solder: A. S. Zuruzi[1]; *S. K. Lahiri*[1]; [1]Institute of Materials Research and Engineering, 10 Kent Ridge Crescent 119 Singapore

Interfacial morphology of the intermetallics formed during the reflow operation has an important effect on the wettability of the underbump metallurgy and reliability of the solder joints. Evolution of the interfacial morphology during reflow is therefore of considerable interest for scientific as well as technological reasons, particularly from the viewpoint of reworking of assembled components. With the present trend towards smaller and lighter electronic components, there is currently a need in the microelectronics industry for direct attachment of chip to organic substrates using the flip chip bonding technique. However, the use of organic materials requires lower reflow temperatures during the assembly process than that needed for reflowing conventional high Pb solder on chip terminal pads. Use of eutectic Pb-Sn solder with electroless nickel underbump metallurgy, instead of the usual copper based metallurgy, is one of the methods which has recently been the subject of investigation by a number of researchers for implementing a low temperature reflow process[1,2]. This paper will address and compare the evolution of the interfacial morphology during reaction of eutectic Pb-Sn solder with electroless nickel and copper. 1. J. Kloeser, K. Heinricht, K. Kutzner, E. Jung, A. Ostman, E. Zakel, and H. Reichl, Proc. ECTC, pp. 254-264 (1997). 2. J.W. Wang, P.G. Kim, K.N. Tu, D.R. Frear, and P. Thomson, J. Appl. Phys., 85, 8456-8463 (1999).

9:15 AM Invited

Wetting of Low Melting Point Alloys on Metal Substrates: *Timothy J. Singler*[1]; Stephan J. Meschter[1]; [1]SUNY Binghamton, Mech. Eng., Binghamton, NY 13902-6000 USA

The wetting dynamics of low melting point alloys on metal substrates is assessed using drop spreading. We observe a primary wetting regime characteristic of many inert liquid systems and a secondary spreading regime characteristic of product-forming reactive systems. We study the influence of temperature, and discuss its effects on several interesting spreading phenomena including the appearance of transient solid phases. We explore the role of surface coatings, particularly their effects on wetting kinetics and contact line morphology.

9:35 AM

Application of Soldering in Partial Melting Zone to Grid Area Package Using Pb Free Hyper-Eutectic Solders: *Jun Seok Ha*[1]; Jae Yong Park[1]; Jae Pil Jung[2]; Choon Sik Kang[1]; [1]Seoul National University, Matls. Sci. & Eng., Shillim-dong, Kwanak-gu, Seoul 151-742 South Korea; [2]University of Seoul, Matls. Sci. & Eng., Jeonnong-dong, Dongdaemun-gu, Seoul South Korea

Unlike the conventional soldering process, the partial melting soldering method is performed above the eutectic temperature and between the eutectic point and the liquidus line. Because it is carried out in the mushy zone, the liquid and the solid phases co-exist. This method will enable us to use other alternative solders than the ones with eutectic composition and thus accelerate development and application of new lead-free solders by offering us a broader range of alternatives. In this study we applied lead- free hyper-eutectic solders (Sn-Bi Sn-In and Sn-Ag) to the partial melting soldering method and investigated the possibility of bonding, metallurgical characteristics and microstructural evolution. A grid array-type substrate was fabricated for soldering in drying oven and conventional reflow soldering machine with hot-air reflow type. Various solder compositions were used in the liquid-solid interface region and experiments were carried out in several temperature ranges. To determine wettability between partial melted solder and Cu substrate, wetting analysis test was conducted at each composition-temperature variable set, and also the test results were compared with the case of full melted solder. After soldering, Scanning Electron Microscope (SEM was used for observation of microstructure and its evolution during aging. To check the soldered joint strength, shear and tensile tests were performed.

9:55 AM

The Possibility of Soldering in Partial Melting Zone Using Hyper-Eutectic Sn-Pb Alloys: *Jae Yong Park*[1]; Jun Seok Ha[1]; Jae Pil Jung[2]; Choon Sik Kang[1]; [1]Seoul National University, Matls. Sci. & Eng., Shillim-dong, Kwanak-gu, Seoul 151-742 South Korea; [2]University of Seoul, Matls. Sci. & Eng., Jeonnong-dong, Dongdaemun-gu, Seoul South Korea

Conventional soldering technology is performed above the full melting temperature region of low melting point solders; the massive trend toward Pb-free solders is not free from this type of temperature restraint in terms of the choice of usable solders. The temperature limit narrows down the choice of usable alternatives to Sn-Pb solders to tin-based alloys with eutectic or near eutectic composition. Off-eutectic alloys, however, with a high temperature liquidus line can be also used as solders in the partial melting temperature zone. The liquid state and the solid state coexist in the partial melting temperature zone, and the portion of liquid state is determined by the lever rule in the phase diagram. To investigate the possibility of soldering in the partial melting temperature zone, the hyper eutectic Sn-Pb alloys and Cu plates were interconnected in the temperature range between the eutectic temperature and liquidus temperature. Drying oven and conventional reflow soldering machine with hot-air reflow type were used. To verify the joint state, a microstructural observation was carried out using Scanning Electron Microscope (SEM). Shear test was conducted to check the strength of the soldered joint interconnected in the partial melting temperature zone. The test results showed a sustainable strength of joint between hyper-eutectic solders and Cu substrate interconnected in the partial melting temperature zone.

10:15 AM Break

10:30 AM Invited

Development of Fluxes for Lead-Free Solders: *Semyon Vaynman*[1]; Morris E. Fine[1]; [1]Northwestern University, Dept. of Matls. Sci. and Eng., Evanston, IL 60208 USA

New lead-free solders, that contain zinc are promising candidates to replace near-eutectic tin-lead solders, because these solders have lower melting temperatures than those based on the tin-silver eutectic, posses good mechanical and fatigue properties and are less expensive than other alternatives to lead containing solders. However, the contact angle on copper for Sn-Zn solders is rather high when utilized with fluxes used for Sn-Pb solders. A novel approach for flux development to improve wetting of copper surface by tin-zinc eutecticis uses tin containing organic compounds as an additive. These metallo-organics decompose at soldering temperatures and produce metallic tin on the surfaces to be soldered. This process improves wetting of copper surface by molten tin-zinc eutectic.

10:50 AM

Reliability Investigation of Printed Wiring Boards Processed with Water Soluble Flux Constituents: *W. Jud Ready*[1]; Laura J. Turbini[1]; [1]Georgia Institute of Technology, Matls. Sci. and Eng., 778 Atlantic Dr., Atlanta, GA 30332-0245 USA

An investigation was conducted to evaluate the effect on reliability of water soluble flux and fusing fluid constituents used in the manufacture of electronic product. The purpose of this program was to determine the mean-time-to-failure (MTTF) of FR-4 substrates processed with three different water soluble flux formulations. The fluxes incorporated hydrochloric acid, hydrobromic acid, a polyglycol and a polyether. In order to determine the MTTF for conductive anodic filament (CAF) growth a test coupon with variable hole-to-hole spacings was used. The variables being studied were (1) flux type, (2) conductor spacing and (3) operating voltage. Quantification of the effect of these variable is determined through a series of MTTF tests. In addition to the electrical measurements, optical and scanning electron microscopy (SEM) is used with energy dispersive X-ray spectroscopy (EDS) to determine the chemical nature of the CAF.

11:10 AM

Effect of Plasma Cleaning on the Flip-Chip Bonding Properties of Si-Wafer/Bumps/Glass System: *Soon Min Hong*[1]; Chang Bae Park[2]; Jae Yong Park[1]; Jae Pil Jung[2]; Choon Sik Kang[1]; [1]Seoul National University, Divi. of Matls. Sci. and Eng., Shillim-dong, Kwanak-gu, Seoul 151-742 Korea; [2]University of Seoul, Matls. Sci. & Eng., Jeonnong-dong, Dongdaemun-gu, Seoul, South Korea

The flip chip provides the highest packaging density and performance and the lowest packing profile among other assembly methods. As the packaging density grows high, however, the cleaning of flux used in conventional process becomes increasingly difficult. The flux residue can seriously affect the reliability and performance of flip chip assemblies by corrosion. In addition, the chemical solvent for flux

cleaning process can also cause the environmental problem which is a world-wide concern in recent years. The purpose of this research is to evaluate the fluxless flip chip bonding properties between Si wafers and Au-coated glass substrates in optical recording media application using Sn-Pb, Sn-Ag, Sn-Bi micro solder bumps. The solder bumps were electroplated on the UBM(Cr/Cu)-deposited Si wafer and reflowed. The pitch of the bumps was 50-150¥ ìm. Instead of flux, we used the Ar plasma cleaning to remove the oxides and other contaminants of solder bumps and glass substrates before flip chip bonding. The wettability of the Au-coated glass and UBM-coated Si wafer were estimated by meniscograph method and area of spread method. The mechanical properties of the joint were examined by micro defect analysis and micro tensile test. The bonding properties were compared with those of the bonding process using flux. The cross section of the solder joint and the intermetallic compounds between solder and coating materials were analyzed by optical microscopy and SEM. The effect of flip chip process parameters, such as temperature profile, conveyor speed and atmosphere, on the bonding properties were also discussed.

11:30 AM

Characteristics of the Sn-Pb Eutectic Solder Bump Formed via Fluxless Laser Reflow Soldering: Jong-Hyun Lee[1]; Jong-Tae Moon[2]; Yong-Ho Lee[1]; *Yong-Seog Kim*[1]; [1]Hong Ik University, Metallu. and Matls. Sci., Sangsu-dong Mapo-Cu, Seoul Korea; [2]Hyundai Electronics Company, Device and Semiconductor Rsch. Div., Ichon 467-701 Korea

With concerns on the environmental contamination and the reliability of the electronic devices, many attempts were made to develop a fluxless reflow soldering process in electronic packaging. In this study, the fluxless reflow soldering was conducted via heating the solder bump using CO_2 laser under controlled atmosphere. A solder disk was placed on the pre-tinned contact pad of the Si wafer and heated with the laser for reflow bumping. The effects of heat input, reflow soldering atmosphere, solder compositions on the mechanical properties and thermal stability of the solder bump were investigated. The heat input to a solder bump was changed from 20 to 60 J and the soldering atmosphere argon, helium, nitrogen, and air. The solders used were Pb-Sn eutectic solder, Pb-Sn composite solder reinforced by in-situ Cu6Sn5 dispersoids, and Sn-3.5%Ag. The reflow soldering under argon helium, nitrogen atmosphere resulted in spherical reflowed bumps. Microstructural observation of the reflowed bump showed a very thin intermetallic layer formed at the solder/contact pad interface. Higher heat inputs resulted in an excessive dissolution of the contact pad metals and lower heat inputs in an insufficient reflow. Shear strengths of the reflowed solder joints measured were equal to those of the reflowed joints formed in a furnace. A study on the mechanisms of the fluxless reflow soldering via the laser heating were conducted by measuring the oxygen concentration distribution in the solder bump by Auger Electron Spectroscopy as well as by estimating the thermal stress developed during the laser heating by thermal modeling of the solder bump.

11:50 AM Invited

Measurements of Metal/Polymer Adhesion Strengths in Microelectronic Packaging: *Jin Yu*[1]; [1]Korea Advanced Institute of Science and Technology, 3373-1 Kusong-dong Yusing-ku, Taejon, Korea

In plastic packages, residual stresses arising from thermal mismatches or pressures exerted by vaporized moisture often lead to the delamination of metal/polymer interfaces. Modifications of polymer surfaces by rf plasma and oxidation treatments of metal surfaces before joining dissimilar materials are commonly used to enhance the adhesion strength of the interface, which is measured by a plethora of techniques. In the present analysis, adhesion strength of Cu/Polyimide and Cu-based leadframe/epoxy were measured using the peel test, pull-out test, and several fracture mechanics tests, and effects of the plasma and oxidation treatments and near the crack tip stress states were investigated. Then, correlations between the peel strength, pull strength and the interface fracture toughness were presented, and the relations among the peel strength, interface fracture toughness and the work of adhesion were discussed based on the X-ray measurements of plastic dissipation and the theoretical analysis.

Pressure Technology Applications in the Hydrometallurgy of Copper, Nickel, Cobalt and Precious Metals: Process Design and Engineering Considerations in High Pressure Hydrometallurgy

Sponsored by: Extraction & Processing Division, Copper, Nickel, Cobalt Committee

Program Organizers: James E. Hoffmann, Hoffmann and Associates, Houston, TX 77242 USA; Norbert L. Piret, Piret & Stolberg Partners, Duisburg 47279 Germany

Monday AM — Room: Lincoln C
March 13, 2000 — Location: Opryland Convention Center

Session Chairs: Jussi Asteljoki, Outokumpu Oy, Corporate Res. & Dev., Espoo 02201 Finland; Norbert L. Piret, Piret & Stolberg Partners, Duisburg 47279 Germany

8:30 AM

Process and Engineering Considerations in the Pressure Decopperizing of Copper Refinery Slimes: *James E. Hoffmann*[1]; [1]James E. Hoffmann and Associates Company, P.O. Box 420545, Houston, TX 77242-0545 USA

Oxidative pressure leaching is gradually supplanting all other techniques for the decopperizing of copper refinery slimes. The reasons for this include: much more rapid reactions, more compact equipment, and perhaps most important, a much lower final copper concentration in the decopperized slimes. This paper will first discuss the reactions occurring during decopperizing, the acidity and temperatures encountered and the techniques employed for discharging non condensable gasses. A spreadsheet is provided which allows adjusting the operating conditions depending upon raw (undecopperized) slimes composition, solids concentration, and lixiviant composition. Typical process flowsheets and process equipment flowsheets are provided.

9:00 AM

Optimizing Gas Mass Transfer in Autoclaves: *Peter Forschner*[1]; Stefan Land[1]; Ronald Klepper[2]; [1]EKATO Ruhr-und, Mischtechnik GmbH, Schopfheim, Germany; [2]EKATO Corporation, Salt Lake City, UT USA

In hydrometallurgy, pure gases like oxygen and hydrogen are used for oxidation and reduction. The gases are expensive and therefore should be used efficiently. Non reacted gas can be recycled into the liquid. Historically vortex gassing has been used, i.e. a mixing impeller close to the liquid surface entrains gas from the headspace into the liquid through a gas vortex. Novel and more efficient methods are surface gassing with up pumping impellers and self-inducing gassing impellers. These alternative impeller systems are well established and common in the chemical industry, but have not been used until recently in hydrometallurgy. Gassing impellers act as internal compressors and increase the interfacial surface for a much higher mass transfer compared to alternate methods mentioned. In the paper results from lab and pilot tests and data from operated plants will be presented. The reactions with gases normally take place under moderate to high pressure, therefore a safe enclosure with mechanical seals and the safety “philosophy” is important. Experienced life and replacement cycles will be reported.

9:30 AM

Laboratory Autoclaves for Hydrometallurgical Research: *Fathi Habashi*[1]; [1]Laval University, Dept. of Min. and Metallu., Quebec City G1K7P4 Canada

Laboratory autoclaves for hydrometallurgical investigations are available in a variety of sizes, models, and materials of constructions. They vary in sizes from 25 ml to 2 liters for laboratory studies and 5

to 50 gallons for pilot plant work. They are essential tools for studying aqueous oxidation of sulfide concentrates, dissolution of oxide minerals at high temperature and pressure and hydrothermal precipitation reactions. The maximum pressure and temperature at which any pressure vessel can be used will depend upon the design of the vessel and the materials used in its construction. Since all materials lose strength at elevated temperatures, any pressure rating must be stated in terms of the temperature at which it applies. A review of existing models and their accessories will be given.

10:00 AM Break

10:15 AM

Design Considerations in Autoclaving: *Ir. Herman Pieterse*[1]; [1]Pieterse Consulting Inc., 6321 N. Calle Campeche, Tucson, AZ 85750 USA

The hydrometallurgical route, due to the fact that it often provides increased recovery, reduced air and water pollution, and lower capital costs relative to roasting and smelting, is becoming the preferred route for many metals. The design of autoclave circuits for various metals are discussed. Emphasis is placed on kinetics, energy balance, heating, cooling, retention, mixing, mass transfer, letdown, pumping, materials of construction, equipment selection. The leaching of copper, as one of the few applications where autoclaving has not been widely applied is highlighted.

10:45 AM

Titanium Clad, High Pressure Acid Leach Autoclaves for Nickel Laterite Ore Processing: *George A. Young*[1]; [1]Dynamic Materials, Metallu. Dept.

High pressure, acid leach autoclaves have been recently installed in Australia to process laterite ores of nickel. As a preferred design over brick/lead lining all three projects have used titanium clad (integral lined), carbon steel pressure vessel autoclaves. The design features horizontal, chambered vessels with agitation. Based on various factors including ore chemistry all three projects specified different grades of titanium, i.e., gd. 1, gd. 11 and grade 17. This paper will review some of those grade selections decisions disclosed by the owners. Additionally, performance of the titanium grades may be difficult to determine with one year or less service but some autoclave internal inspections have been conducted. Comments from the operators on autoclave and material performance will be included. Dynamic Materials, Inc., Lafayette, CO supplied the titanium-clad steel for the autoclave vessels for two of three projects, Bulong and Murrin-Murrin. ASC-E, Adelaide Australia fabricated the vessels for all three projects including Cawse. Several other projects are awaiting final approval to proceed.

Surface Engineering in Materials Science I: Coatings/Films Synthesis and Processes (SP)-I

Sponsored by: Materials Processing and Manufacturing Division, Surface Engineering Committee

Program Organizers: Sudipta Seal, University of Central Florida, Advanced Materials Processing and Analysis Center and Mechanical, Materials and Aerospace Engineering, Orlando, FL 32816 USA; Narendra B. Dahotre, University of Tennessee Space Institute, Center for Laser Applications, Tullahoma, TN 37388 USA; Brajendra Mishra, Colorado School of Mines, Kroll Institute for Extractive Metals, Golden, CO 80401-1887 USA; John Moore, Colorado School of Mines, Department of Metallurgy and Materials Engineering, Golden, CO 80401 USA

Monday AM — Room: Canal B
March 13, 2000 — Location: Opryland Convention Center

Session Chairs: I. Manna, IIT, Metallu. and Matls. Sci. and Eng., Kharagpur, WB 721302 India; Brajendra Mishra, Colorado School of Mines, Adv. Coatings and Surface Eng. Lab. Dept., Golden, CO 80401-1887 USA

8:30 AM

Oxidation-Resistant Coatings for Molybdenum Electrodes: *Sury Challapalli*[1]; Earl Hixson[1]; John Moore[1]; [1]Colorado School of Mines, Adv. Coati. and Surf. Eng. Lab., Dept. of Metallu. and Matls. Eng., Golden, CO 80401-1887 USA

The high-temperature oxidation resistance of molybdenum can be significantly improved by coating it with MoSi2. But, at the high temperature of operation, silicon from MoSi2 diffuses into the molybdenum substrate and the oxidation resistance of the system deteriorates. Further, because of the CTE mismatch between Mo and MoSi2, the composite breaks down and spalls on thermal cycling. To alleviate the problem of the CTE mismatch, the CTE of MoSi2 is matched with that of Mo by the addition of 50 wt% SiC. But, the problem of silicon (and now additionally carbon) diffusion into the molybdenum substrate persists, changing the chemistry of the overlayer and deteriorating the oxidation resistance of the composite. Incorporating a diffusion barrier layer between the Mo substrate and the MoSi2+SiC composite layer on the top solved this problem. The newly developed amorphous diffusion barrier layer prevents diffusion of both carbon and silicon into the substrate. A number of problems still need to be resolved with respect to the diffusion barrier layer. These concern the chemistry, thermal stability, crystallization behavior, and cyclic oxidation resistance. Finite element modeling studies are also being undertaken to determine the optimal thickness of the individual layers, and the compositional gradient of the MoSi2+SiC composite to provide a tolerable residual stress level and also for optimal distribution of that stress in the overall coating system. These results will be utilized to optimize the diffusion barrier layer thickness. The present talk will review the recent results obtained and highlight the future investigations. Supported by NSF under DMR Award # 9730775.

8:50 AM Invited

Synthesis of Nanocrystalline Inconel 625 Powders by Cryomilling: *Degang Cheng*[1]; Rudy Rodriguez[1]; Mike Ice[1]; E. J. Lavernia[1]; [1]University of California Irvine, Dept. of Chem. and Biochem. Eng. and Matls. Sci., Irvine, CA 92697-2575 USA

The present paper report on a successful synthesis of nanocrystalline Inconel 625 powders by cryogenic high-energy ball milling (cryomilling). Commercially available Inconel 625 powders (Diamalloy 1005 AMDRY 625) is milled in liquid nitrogen for 8 hours. The characteris-

tics of the milled powders, i.e., morphology, self-agglomeration, powder size, grain size and structure evolution during milling, were analyzed using X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

9:15 AM Invited

Film Formation on Metals and Alloys by Thermal, Electrochemical and Plasma Oxidation: *D. L. Cocke*[1]; S. Promreuk[1]; D. G. Naugle[2]; R. B. Schennach[1]; [1]Lamar University, Gill Chair of Chem. and Chem. Eng., P.O. Box 10022, Beaumont, TX 77710 USA; [2]Texas A&M University, Dept. of Physics, College Station, TX 77840 USA

Interfacial oxidation is an established approach to produce surface thin films for catalysts, corrosion and ware protective coatings, and electronic structures. The three main methods, thermal, anodic and plasma, for oxidation of metallic substrates still lack an adequate fundamental physical-chemical models, that can allow film design, particularly on alloys. Oxidation of alloys produce multicomponent oxides with quite different structures depending on the conditions and the methods of oxidation. The three methods will be discussed in terms of physical/chemical parameters that influence the chemical nature and structure of the resulting oxides. The electrochemical processes that occur during the materials reaction with a chosen environment will be used to discuss the physical and chemical mechanisms involved. Intrinsic and extrinsic electric fields will be shown to influence the chemical and structural nature of the resulting oxide structures. Surface analysis results [XPS (X-ray Photoelectron Spectroscopy) and ISS (Ion Scattering Spectrometry)] from the three oxidation methods applied to metals and their binary and ternary alloys will be discussed. The resulting structures on the ternary and binary alloys will be discussed in terms of an evolving electrochemical model.

9:40 AM

Study of Operating Conditions on Electroless Plating of Nickel for MEMS Application: *Jin Huh*[1]; Jae-Ho Lee[1]; [1]Hong Ik University, Dept. of Metallu. Eng. and Matls. Sci., Seoul 121-791 Korea

Electroless depositions of nickel were conducted in different bath conditions to find optimum conditions of electroless nickel plating for fabrication of micro structures in MEMS applications. In LIGA or LIGA-like process, the operating temperature and pH is restricted and optimum operating conditions were different from conventional electroless deposition of nickel. And then to find optimum conditions, the effects and selectivity of activation method on several substrates were investigated. The effects of nickel salt concentration, reducing agent, complexing agent and inhibitor on deposition rate was investigated. The effect of pH on deposition rate and content of phosphorous in deposited nickel was also observed. In optimum operating bath condition, deposition rate was 7?/hr at 60? and pH 10.0. The rate was decreased with stabilizer concentration. And then micro structures were fabricated with optimum bath condition.

10:00 AM

Electron Beam Enhancement of Composite Coatings: *Vadim J. Jabotinski*[1]; Francis H. (Sam) Froes[1]; [1]University of Idaho, Instit. for Matls. and Adv. Process., Moscow, ID 8384-3026 USA

Electron beam processing offers great technical and economic capabilities of improvement of composite coatings. Heating combined with radiation treatment offering by the electron beam processing allows novel changes and modification in coating materials. This paper will consider fundamentals and applications of the electron radiation in processing traditional and advanced coating materials including high-temperature superalloy-, intermetallic-, and ceramic-matrix composites applied by conventional techniques such as thermal spraying, high velocity oxygen fuel, plasma, laser, and physical and chemical vapor deposition. The specific effects leading to increase in the coating lifetime and wear, heat, and corrosion resistance will be identified. Possible mechanisms for increasing the toughness, adhesion, bond strength and reducing porosity and cracks will be discussed.

10:20 AM Break

10:35 AM

Modeling of Combustion Flame Assisted Chemical Vapor Deposition of Diamond Thin Films: *J. Kapat*[1]; K. Elshot[1]; [1]University of Central Florida, Dept. of Mech., Matls. & Aero. Eng., Orlando, FL 32816-2450 USA

Combustion flame assisted chemical vapor deposition (CFCVD) is of interest to researchers because of its simplicity. The main advantages of this method over other CVD methods include higher growth rates, low cost, and the potential to deposit a large area. In this study, a numerical model has been developed for analyzing chemically reacting flow, mass and heat transport and reactions in CFCVD of a diamond thin film with a laminar, premixed C2H2/O2 flame. This model is used to numerically investigate the effect of different process parameters on the growth rate of the thin film. In this model, the flame is held perpendicular to a Si substrate, where the film is deposited. The temperature of the substrate is controlled independent of the flame temperature as the substrate is attached to an externally cooled copper substrate. As would be discussed later, the substrate is placed within the feather region of the flame for optimum diamond deposition. Chemical model discriminates between graphitic and diamond phases through the use of different surface reactions so as to model the differential etch and growth rates of these two phases. The focus of this paper is to present the effect of inlet gas composition and substrate to flame nozzle distance on thin film deposition rate.

10:55 AM

Process Parameter Selection Rules and Direction of Maximum Stress for Laser-Deposited Coatings: *A. Kar*[1]; Franz-Josef Kahlen[1]; [1]University of Central Florida, Laser-Aided Manu., Matls. and Micro-Process. Lab., Schl. of Optics and Ctr. for Rsch. and Edu. in Optics and Lasers, Mech., Matls., and Aero. Eng. Dept., Orlando, FL 32816 USA

This paper presents a set of design rules for a laser-aided powder deposition process. A high power CO2 laser is used to melt the powder and deposit a coating on a substrate. Dimensionless numbers characterizing this powder deposition process are identified using Buckingham's P-Theorem. These dimensionless numbers are used to identify a range of values for the process parameters, such as the laser beam power, spot diameter, substrate translation speed and powder flow rate, to achieve good quality coatings for different coating materials. The yield and ultimate strengths are examined for stainless steel 304 (SS 304) coatings for three different processing conditions. These stresses are related to the dimensionless similarity parameters through the operating conditions and physical dimensions of the deposit. Experiments conducted for SS 304 shows that the yield strengths are close to the value of wrought material. Ultimate strengths are within 80% of the corresponding values for wrought SS 304. The yield strength is found maximum in a given direction and this direction is oriented very close to the direction of material solidification. A mathematical model is derived to calculate the residual stresses created during solidification, accounting for directionally preferred solidification.

11:15 AM

Time-Dependent Relationships between Hf Dopant Incorporation and HfCl4 Precursor Concentration during CVD-NiAl Diffusion Coating Growth: *G. Y. Kim*[1]; Limin He[1]; Justin D. Meyer[1]; W. Y. Lee[1]; [1]Stevens Institute of Technology, Dept. of Chem., Biochem. and Matls. Eng., Castle Pt. on Hudson, Hoboken, NJ 07030 USA

The incorporation behavior of Hf as a beneficial dopant during aluminizing of a single crystal Ni alloy has been studied using a laboratory-scale CVD reactor which can be mathematically modeled while emulating the actual manufacturing environment. The effects of proactively varying the gas phase concentration of the dopant precursor (HfCl4), as a function of aluminizing time, on the concentration and distribution of Hf in the NiAl coating matrix were examined to understand the dynamic nature of the Hf doping process. Also, the process parameters and reactor conditions which led to the formation of Hf-rich particles and experimental irreproducibility were identified. These results will be discussed in the context of increasing the scale adhesion behavior of the Hf-doped NiAl coating, through model-based process optimization, for thermal barrier coating applications.

Teaching Electronic, Magnetic and Optical Materials: A Symposium in Memory of Professor Gregory E. Stillman: Session I

Sponsored by: Electronic, Magnetic & Photonic Materials Division, Education Committee
Program Organizer: Mark A. Palmer, Virginia Commonwealth University, Richmond, VA 23284-3015 USA

Monday AM — Room: Bayou D
March 13, 2000 — Location: Opryland Convention Center

Session Chair: Mark Palmer, Virginia Commonwealth University, Richmond, VA 23284-3015 USA

8:30 AM Opening Remarks
Mark Palmer, Session Chair;
Robert Stull, Chair EMPMD

8:40 AM
A Brief Summary of Professor Stillman's Contributions: John Parsey

8:45 AM Keynote
Bringing Electronic Materials to the Forefront of Engineering Education: *Emily L. Allen*[1]; [1]San Jose State University, Dept. of Chem. and Matls. Eng.

The design, selection, and processing of materials has always been critical to the practice of all engineering disciplines. As the study of traditional metallurgy transformed into the discipline of materials science and engineering, a marriage with solid state physics and chemistry occurred which brought new types of materials into being and allowed the unification of the discipline under the themes of structure, properties and processing. With the rise of the electronic age, the importance of electronic, photonic and magnetic materials has skyrocketed in economic importance as well as in scientific and engineering advances. MS&E curricula, and the service courses we offer to other programs, have not always kept pace with the increased importance of electronic materials. At San Jose State, we have initiated new courses and programs in electronic materials, utilizing the appropriate structure, properties, and processing approaches through laboratory experience. I will describe our electronic materials courses for Materials Engineering majors as well as our service courses for Electrical, Computer and Chemical Engineering majors. Our new degree in Microelectronics Process Engineering will be highlighted as well. I will stress the learning styles-based pedagogical methods used to enhance the learning environments of various courses.

9:30 AM Keynote
Applets and Dynamic Multimedia Objects for Teaching and Learning: *Chu R. Wie*[1]; [1]State University of New York, Buffalo, NY USA

Professor Chu is the Director for the Center for Active Learning of Microelectronics and Photonics at SUNY Buffalo, where he has developed "Educational Java Applets in Solid State Materials," he is also the Chair of the 2000 International Conference On Simulation and Multimedia in Engineering Education Conference which will bring together experts and colleagues who are interested in the fast growing area of modeling (both analytical and computational), simulation and visualization (and their comparison with experiments and observations), and simulation and multimedia-based engineering education. He will discuss his experience in developing these modules, using them in the classroom, and the activities of others as presented at the conference.

10:15 AM Break

10:30 AM
Microtechnology Education: Semiconductor and Mems Processing for Undergraduate and Graduate Students at the University of Washington: *T. G. Stoebe*[1]; T. P. Pearsall[1]; J. W. Rogers[2]; R. B. Darling[3]; M. Afromowitz[3]; P. Yager[4]; [1]University of Washington, Matls. Sci. and Eng., Seattle, WA 98195-2120 USA; [2]University of Washington, Chem. Eng. Dept., Seattle, WA 98195-2120 USA; [3]University of Washington, Elect. Eng. Dept., Seattle, WA 98195-2120 USA; [4]University of Washington, Bioeng. Dept., Seattle, WA 98195-2120 USA

An NSF-sponsored Combined Research and Curriculum Development project has allowed a team of faculty members at University of Washington to develop a series of courses and laboratories for students interested in microtechnology. A sophomore class introduces students to electronic materials properties and processing; while a junior laboratory provides an introduction to clean room processes and equipment. A senior level class on semiconductor processing includes a laboratory in which the students make a MOSFET device. Graduate level courses include an introduction and laboratory class in MEMS and a process integration class. Details on course curricula and laboratory development will be presented with lessons learned and advice for the development of similar programs. This program is supported by the National Science Foundation.

11:00 AM Invited
Introduction of Electronic Materials to Undergraduate Students in Materials Engineering: *Matthias Militzer*[1]; [1]The University of British Columbia, Dept. of Met. and Matls. Eng., Vancouver, BC V6T1Z4 Canada

Electronic materials are taught to undergraduate students in materials engineering at the University of British Columbia as a two credit elective course in the fourth year. Since the students have in general no background in quantum physics, the course is based on a predominantly descriptive approach to the subject with the objective being to develop an understanding of basic concepts of specifications and making of semiconductor materials and devices. Semiconductor materials are introduced in relation to other materials (metals, ceramics, etc.) which are stronger emphasized in the current curriculum. It is delineated why silicon is the material of choice. To motivate learning the basics of electronic materials, selected optical and electronic devices (transistors, photodetectors, etc.) are introduced throughout the course. An integral part of the course is to incorporate research aspects by a site visit to laboratory facilities (molecular beam epitaxy, clear room, etc.) and presenting selected results of research conducted by the instructor or guest lecturers (e.g. on misfit dislocations). Further, assignment work is included to perform simple calculations of materials aspects in the electronic industry.

11:30 AM Invited
Materials Science Education for the Information Age: *Sharmila M. Mukhopadhyay*[1]; [1]Wright State University, Dept. of Mech. and Matls. Eng., Dayton, OH 45435 USA

Materials science, though regarded as an interdisciplinary field, has historically evolved from metallurgy and this influence is very clear in the traditional "materials" courses offered in most places. The typical focus is normally on the interconnected chain linking processing-structure-properties-performance, each link stressing more on mechanical & structural aspects than on any other. In this presentation, some ideas of possible additions and alterations to the existing curricula will be presented. These examples range from freshmen level experiments across the entire engineering curriculum to focused graduate (or upper-level undergraduate) courses such as "Electroceramics," "Electric Materials," etc. that the author has introduced. Student responsiveness, degrees of success and special challenges will be discussed on a case by case basis.

Ultrafine Grained Materials: Fundamentals and Process Mechanisms: I

Sponsored by: Materials Processing and Manufacturing Division, Powder Metallurgy Committee, Shaping and Forming Committee

Program Organizers: Rajiv S. Mishra, University of Missouri, Metallurgical Engineering, Rolla, MO 65409-0340 USA; S. L. Semiatin, Wright Laboratory, Materials Directorate, Dayton, OH 45440 USA; C. Suryanarayana, Colorado School of Mines, Department of Metal and Materials Engineering, Golden, CO 80401 USA; Naresh Thadhani, Georgia Institute of Technology, School of Materials Science and Engineering, Atlanta, GA 30332-0245 USA

Monday AM — Room: Polk A/B
March 13, 2000 — Location: Opryland Convention Center

Session Chair: S. Lee Semiatin, Air Force Research Laboratory, Wright-Patterson Air Force Base, OH 45433-7817 USA

8:30 AM Introductory Remarks

8:35 AM Invited
Grain Boundaries of Nanophase Alloys Prepared by Mechanical Attrition: *Brent Fultz*[1]; Heather N. Frase[1]; [1]California Institute of Technology, Div. Eng. Appl. Sci., Mail 138-78, 1201 E. Calif. Blvd., Pasadena, CA 91125 USA

We report results on the structures of grain boundaries in nanocrystalline materials prepared by high energy ball milling. Results are reported on average widths of grain boundaries, as determined from a combination of Mossbauer spectrometry measurements in conjunction with grain size measurements by x-ray lineshape analysis and TEM dark field imaging. More recently we have used small angle neutron scattering to measure the densities of atoms and magnetic moments within grain boundaries of nanocrystalline fcc Ni_3Fe. Both densities are suppressed within the grain boundaries in comparison to bulk material. From the nuclear scattering measured by SANS, we find a distribution for the atom density in the grain boundary. Curiously, by quenching nanocrystalline samples to low temperature we can alter somewhat the grain boundary density. Quenching causes a change in the atomic density of the grain boundaries, indicating a more discontinuous transition in density between grain boundary and bulk material.

9:00 AM Invited
Localized CVD and the Ultrafine Grain Structure: *Harris L. Marcus*[1]; Shay Harrison[1]; Leon Shaw[1]; James E. Crocker[1]; Lianchao Sun[1]; [1]University of Connecticut, Instit. of Matls. Sci., Storrs, CT 06269-3136 USA

In high rate localized chemical vapor deposition using a laser beam to thermally decompose gas precursors the resulting grain size ranges from the near amorphous to a continuum of ultrafine grain sizes depending on processing parameters. This paper will describe the nature of the grain sizes for various ceramic materials as a function of processing and postprocessing conditions. The grain size characterizations were performed using Raman spectroscopy, NMR, TEM, X-ray and other analytic approaches. The results will be described in terms of the various characterization approaches and related to modeling of the processing variables.

9:25 AM Invited
Chemical Vapor Synthesis of Nanostructured Powders and Their Properties: *Horst W. Hahn*[1]; [1]Darmstadt University of Technology, Matls. Sci. Dept., Thin Films Div., Petersenstr. 23, Darmstadt 64287 Germany

Chemical Vapor Synthesis and Low Pressure Flame Synthesis offer exciting opportunities for the preparation of nanocrystalline ceramic powders with excellent control of the particle size, size distribution, degree of agglomeration, morphology and elemental distribution in the individual nanoparticles. In addition, porous and dense nanocrystalline coatings with functional gradients can be obtained starting from the same metalorganic precursors. The design opportunities are similar to those common in CVD processing of thin films. The synthesis method will be described including a model for the growth of primary particles and agglomerates. The resulting properties of nanocrystalline doped, two phase and coated ceramic composites will be discussed.

9:50 AM
Synthesis and Characterization of Mechanically Amorphized and Shock Densified Nanocrystalline NiTi Alloy: *Xiao Xu*[1]; Naresh N. Thadhani[1]; [1]Georgia Institute of Technology, School of Matls. Sci. and Eng., 778 Atlantic Dr., Atlanta, GA 30332-0245 USA

In this study, mechanical amorphization (MA) and shock compaction (SC) experiments were performed on pre-alloyed Nitinol powders as well as elemental Ni and Ti powder mixture to prepare bulk nanocrystalline alloy compacts. The MA experiments were conducted using a SPEX 8000 mixer/mill. The pre-alloyed powders were ball-milled in an Ar atmosphere and the elemental powders were alloyed using Hexane. The SC experiments were performed using a single-stage gas gun at peak pressure of 5-9 GPa. The pre-alloyed compact showed crystallization to B2 phase with a nano-size microstructure. In contrast, amorphous microstructure was retained in the shocked compact of elemental mixture, which crystallized to nanocrystalline NiTi B2 phase during post-shock thermal treatment. In this paper, we will present the results of shock densification and microstructural characteristics of the nano-structure formed in the bulk NiTi compacts. Research funded by ARO under Grant No.DAAG55-97-1-0163.

10:10 AM
Synthesis and Characterization of Ultrafine Ti Powders: *S. Amarchand*[1]; T. R. Ramamohan[1]; P. Ramakrishnan[1]; [1]Indian Institute of Technology, Dept. of Metallu. Eng. and Matls. Sci., Bombay 400076 India

The present work deals with a novel chemical solution synthesis route, for the preparation of nanosize Ti powders, from Titanium dioxide. Titanium dioxide is allowed to form a complex, titanium catecholate precursor, in presence of ammonium sulphate and concentrated sulphuric acid. The complex is filtered, washed with cold isopropyl alcohol and dried. Hydrogenation of titanium catacholate is carried out for different durations at various temperatures. Titanium hydride is prepared by heating the titanium catacholate precursor at 800°C in a furnace of 8E-6 torr vacuum and dehydrogenated in vacuum to get fine Ti powders. The characteristics evaluated by XRD, SEM and TEM indicated that the powders are pure Titanium with crystallite size in the range 45-60 nm.

10:30 AM Break

10:40 AM Invited
Magnetization Reversal in Nanocomposite Exchange Spring Magnets Observed Directly with a Magneto-Optical Indicator Film: *Robert D. Shull*[1]; Alexander J. Shapiro[1]; Henrietta J. Brown[1]; Valerian I. Nikitenko[2]; Vladimir S. Gornakov[2]; J. Samuel Jiang[3]; A. Inomata[3]; C. H. Sowers[3]; Samuel D. Bader[3]; [1]NIST, Metallu. Div., 100 Bureau Dr., MS 8552, Gaithersburg, MD 20899-8552 USA; [2]Institute of Solid State Physics, Russian Acad. of Sci., Chernogolovka, Russia; [3]Argonne National Laboratory, MSD 223, 9700 S. Cass Ave., Argonne, IL 60439-4845 USA

Epitaxial Sm-Co (350 Å)/Fe(500 Å) bilayer films were grown on Cr (200 Å) buffered MgO (100) substrate by sputtering. Magnetic hysteresis loops measured in a SQUID magnetometer showed characteristic exchange-spring behavior where the reversal of the soft Fe layer is pinned at the interface by the SmCo hard layer. For the first time in such a material, the remagnetization process was observed directly using the magneto-optic indicator film (MOIF) technique. In order to

investigate the magnetic spin rotation process inside the bilayer during remagnetization, a 0.3 mm hole was made in the sample, and the magnetostatic field (H_{ms}) around the hole was visualized through the intensity changes of the double Faraday effect in a transparent indicator film with in-plane anisotropy. Black and white contrast on opposite sides of the microhole was observed, indicating the direction of magnetization in the sample around the hole. We followed the line of contrast symmetry and analyzed the spin rotation process in the soft ferromagnetic component during remagnetization. This was compared to the macroscopic magnetization as determined by a vibrating sample magnetometer (VSM). Findings include direct observation of spin rotation in opposite directions for field applications slightly off either side of the easy axis of magnetization during conventional field reversal. When the field was aligned with the easy axis, no uniform spin rotation was observed. During rotational hysteresis, a unique spin behavior was observed: spin rotation was discovered to change sign without an accompanying change in the sign of the field rotation. The reasons for these unusual remagnetization observations will be discussed.

11:05 AM

The Relationship between the Reaction Conditions and the Characteristics of the Metal-Bearing Ferrites Produced at Ambient Temperature: *Oscar Juan Perales Perez*[1]; Yoshiaki Umetsu[2]; Atsuo Kasuya[1]; Kazuyuki Tohji[3]; [1]Tohoku University, Ctr. for Interdis. Rsch., Aramaki aza Aoba, Aoba-ku, Sendai 980-8578 Japan; [2]Tohoku University, Instit. for Adv. Matls. Process., Katahira 2-1-1, Aoba-ku, Sendai 980-8577 Japan; [3]Tohoku University, Dept. of Geosci. and Tech., Aramaki aza, Aoba-ku, Sendai 980-8578 Japan

Magnetite and various metal-bearing ferrites were produced directly from aqueous solutions at 25°C by simultaneous control of the oxidizing conditions for co-existing Fe(II) ion and pH. In this presentation, the correspondence between the reaction conditions of formation of the ferrite in sulfate medium and its structural and magnetic characteristics will be discussed. The formation of a Zn-bearing ferrite was selected as a first case study. The precipitates were characterized by XRD, EPMA, FT-IR, HRTEM and magnetic hysteresis loop measurement. Furthermore, the analysis of the local structure of Fe and Zn atoms by Extended X-ray Absorption Fine Structure Spectroscopy (EXAFS) was also undertaken. It was found that the crystallinity, the de-hydration of the intermediate compound and the diminution of the sulfate content in the nano-sized ferrites (average crystallite size 10 nm) could be promoted by: (i) increasing the Fe/Zn mole ratio in the precipitates, (ii) a suitable duration of the aeration of the ferrite precursor suspension under alkaline conditions or, (iii) by aging of the precipitates at 25°C. In turn, EXAFS revealed that the ambient-temperature Zn-bearing ferrite exhibited a similar structure than the ceramic Zn ferrite produced at temperatures above 1000°C and Zn atoms were fully incorporated into the ferrite framework occupying the tetrahedral sites. The mentioned effects were attributed to the suitable progress of the oxidation-hydrolysis reactions of Fe(II) species and the loss of water from the intermediate compound during the formation of the ferrite structure incorporating Zn atoms, which also explained the observed enhancement in the saturation magnetization of the precipitates. The above results enable our proposal to be considered not only as a novel route to synthesize magnetic materials (ferrites) at ambient temperature but also a promising alternative to remove metal ions and produce re-usable precipitates in the treatment of large volumes of polluted effluents.

11:25 AM

Thermal Mechanisms of Grain Refinement in Lath Martensitic Steels: *John William Morris*[1]; Zhen Guo[1]; [1]University of California, Dept. of Matls. Sci., Berkeley, CA 94720 USA

The effective grain size of a martensitic steel with a dislocated lath substructure is the pertinent coherence length. For intergranular fracture this is the prior austenite grain size, for transgranular cleavage, the packet size in the (100) plane, and for slip-dominated processes, the packet size in (110). To achieve exceptional properties, it is important to refine the effective grain size into the submicron range, and it is desirable to do this with thermal processes that can be applied to plate product. Three mechanisms are available. In increasing order of effectiveness they are: alternate thermal cycling to refine the prior austenite grain size and the packet size, intercritical tempering to disrupt lath alignment by interposing thermally stable austenite, and rapid thermal cycles that disrupt packet alignment. The mechanisms of refinement to ultrafine grain size will be discussed. Successful examples of each grain refinement mechanism will be given.

11:45 AM

Kinetics of Glass Formation and Nanocrystallization in Al-RE-(TM) Alloys: *Robert I. Wu*[1]; Gerhard Wilde[1]; John H. Perepezko[1]; [1]University of Wisconsin-Madison, Dept. of Matls. Sci. and Eng., 1509 University Ave., Madison, WI 53706 USA

Aluminum-rich amorphous alloys have attracted considerable attention in recent years for their superior mechanical properties compared with conventional Al-based alloys. Often, the occurrence of a precursor crystallization reaction during heating of rapidly solidified amorphous samples leads to the formation of microstructures with finely dispersed nanocrystalline Al in an amorphous phase and offers effective dispersion strengthening. While many amorphous alloys are produced by rapid solidification processing, mechanical intermixing also provides an alternative route to synthesize metallic glasses. In the present study, characterization results on the Al-based metallic glasses by TEM and modulated-temperature calorimetry (DDSC) indicate that the glassy state has actually been attained by rapid melt-quenching as well as by deformation mixing. Annealing studies on the glassy samples produced by different processing pathways indicate a completely different nanocrystallization behavior and suggest that the quenched-in nuclei originate from the rapid melt-quenching process. Moreover, glass formation appears to be controlled by the suppression of growth of nuclei formed during rapid melt quenching for Al-based systems. With the aim of enhancing the mechanical properties of Al-based nanocrystalline materials, efforts have been focused upon increasing the particle density of nanocrystals by probing the crystallization kinetics of the primary phase. A key issue in the controlled synthesis of nanocrystalline Al microstructures is the capacity to control the nucleation density that appears to be linked to quenched-in, pre-existing clusters. Numerical modeling based upon the size distribution of the primary nanocrystals in partially crystallized $Al_{88}Y_7Fe_5$ samples has been applied to analyze the nucleation kinetics during nanocrystallization in these metallic glasses. In addition, incorporation of insoluble elements (e.g. Pb) during RSP has successfully yielded an increase in the nanocrystal particle density developed during primary crystallization. The discovery has provided new microstructural control in the study of heterogeneous nucleation kinetics in Al-based metallic glasses. The support of the ARO (DAAG55-97-1-0261) is gratefully acknowledged.

AIME/TMS KEYNOTE ADDRESS

Monday, March 13, 2000
11:30 AM - 1:00 PM
Room: Presidential Ballroom

FUTUREVIEW: A Look Ahead
Speaker: Daniel Burrus, Burrus Research Associates, Inc.

Thanks to recent innovations in science and technology we are at the gateway to a renaissance in materials technology, in terms of not only developing new applications, but also in terms of the industry itself. Although we are at a time of tremendous opportunity, we are at the same time faced with problems of equal magnitude. This presentation will provide you with valuable insight into how best to capitalize on present and future opportunities, while artfully minimizing problems along the way.

Advanced Technologies for Superalloy Affordability: Superalloy Modeling-Processing, Microstructure and Property

Sponsored by: Structural Materials Division, High Temperature Alloys Committee

Program Organizers: K. M. Chang, West Virginia University, Mechanical & Aerospace Engineering, Morgantown, WV 26506 USA; K. R. Bain, GE Aircraft Engines, Cincinnati, OH 45215 USA; D. Furrer, Ladish Company, Cudahy, WI 53110 USA; S. K. Srivastava, Haynes International, Kokomo, IN 46904 USA

Monday PM — Room: Canal C
March 13, 2000 — Location: Opryland Convention Center

Session Chairs: Krishna Srivastava, Haynes International, Kokomo, IN 46904 USA; Michael Fitzpatrick, Solar Turbines Inc., Adv. Tech. Matls. and Process., San Diego, CA 92186 USA

2:00 PM Invited

Application of Calphad Methods to Ni-Based Superalloys: *Nigel Saunders*[1]; [1]Thermotech Limited, Surrey Tech. Ctr., The Surrey Rsch. Park, Guildford, Surrey GU25YG UK

Thermodynamic calculations using the CALPHAD route are becoming increasingly used for practical purposes [1]. This paper will describe a number of applications of the methodology to Ni-based superalloys, with particular emphasis on issues associated with affordability. These applications will include its use in helping to define composition specifications, monitoring of sigma formation, critical temperatures and heat treatment windows during processing, more efficient and speedy alloy design and calculation of critical input parameters for use in process modeling. [1] N.Saunders and A.P.Miodownik "CALPHAD-a Comprehensive Guide" (Elsevier Science, Oxford, 1998).

2:25 PM Invited

Phase Compositions in Alloy 718: A Comparison between APT/APFIM Measurements and Thermodynamic Predictions: *M. K. Miller*[1]; S. S. Babu[1]; [1]Oak Ridge National Laboratory, Mets. and Cer. Div., 1 Bethel Valley Rd., Oak Ridge, TN 37831-6376 USA

In order to improve the properties of nickel-based superalloys, it is essential to determine the partitioning behavior of the solute additions within the microstructure. The techniques of atom probe field ion microscopy (APFIM) and atom probe tomography (APT) permit the solute partitioning and compositions of the coexisting phases to be determined with near atomic resolution in these complex engineering alloys. In Alloy 718, these techniques have revealed that the secondary precipitates have a dual nature and are combination of the DO_{22}-ordered $Ni_3(Nb,Ti)$ ' phase and the $L1_2$-ordered $Ni_3(Al,Ti,Nb)$ g' phase. The experimentally determined compositions of these phases will be compared to thermodynamic predictions. This research was sponsored by the Division of Materials Sciences, U.S. Department of Energy, under contract DE-AC05-96OR22464 with Lockheed Martin Energy Research Corp. and through the SHARE Program under contract DE-AC05-76OR00033 with Oak Ridge Associated Universities.

2:50 PM

Capitalizing on Computational Tools in Alloy and Process Development: *Michael G. Fahrmann*[1]; G. D. Smith[1]; [1]Special Metals Corporation, 3200 Riverside Dr., Huntington, WV 25705 USA

Recently computational tools such as Thermo-Calc have been made increasingly use of to expedite alloy development and process improvement, thus cutting cost/time cycles of experimental trials. Three concrete examples are presented illustrating the capabilities of the current modeling software: (1) the development of a new weld wire for automotive exhaust systems, (2) the development of a new alloy for superheater tubing in advanced power plants, (3) the improvement of heat treating processes of high performance alloys. It is emphasized, however, that Thermo-Calc requires from the user also a sound knowledge of the physical metallurgy of the system in order to ensure effective usage of this tool.

3:10 PM

Precipitation of γ' from γ during the Weld Thermal Cycle: Recent Results of APFIM Characterization and Modeling: *S. S. Babu*[1]; S. A. David[1]; J. M. Vitek[1]; M. K. Miller[1]; [1]Oak Ridge National Laboratory, 1 Bethel Valley Rd., Oak Ridge, TN 37831 USA

Welding plays an important role in economical reuse and reclamation of used and failed nickel-base superalloy blades. It has been shown that it is possible to weld these alloys with high-energy processes such as electron beam and laser welding. The microstructure development during weld thermal cycles plays a vital role in the weldability and the service properties. In this paper, the precipitation of γ' phase during simulated weld cooling conditions was studied with transmission electron microscopy and atom probe field ion microscopy and atom probe tomography. The results indicate non-equilibrium alloying elements partitioning between γ and γ' phases. The morphology of γ' precipitates was irregular compared to that of cuboidal shape in the heat-treated condition. The experimental results will be compared with thermodynamic and kinetic calculations. This research is supported by the Division of Materials Sciences, U.S. Department of Energy under contract DE-AC05-96OR22464 with Lockheed Martin Energy Research Corporation.

3:30 PM

Solidification Diagram of Ni-Cr-Fe-Nb System: *Wei Chen*[1]; Wanhong Yang[1]; Keh-Minn Chang[1]; Sarwan K. Mannan[2]; John J. deBarbadillo[2]; [1]West Virginia University, Dept. of Mech. and Aero. Eng., P.O. Box 6106, Morgantown, WV 26506-6106 USA; [2]Special Metals Corporation, 3200 Riverside Dr., Huntington, WV 25705 USA

Macroscopic solidification segregation is one of the key issues in the production of high quality premium ingots of Ni-base superalloys, such as alloys 718, 706 and 625. These commercial alloys contain certain amounts of Nb, which is associated with the formation of eutectic phases like Laves and Ni_3Nb. Quarternary Ni-Cr-Fe-Nb alloy system is selected as the model alloy system to study the fundamentals solidification behaviour of multicomponent industry alloys. Several experimental alloys consisting of various combinations of Cr, Fe and Nb were prepared. The elemental segregation profiles and terminal solidification phases were determined by DTA and SEM-EDS analysis. Two types of eutectic products, Ni_3Nb and Laves, exist in the interdendritic region. A computational thermodynamic software, Thermo-Calc, was employed to calculate the solidification constitution diagram of Ni-Cr-Fe-Nb system. The calculated phase boundaries were verified using experimental results. A simplified thermodynamic database was developed to predict the solidification path and elemental partitioning of the model alloys. The obtained diagram can help to understand the solidification segregation of Nb-containing superalloys with complex chemical compositions.

3:50 PM Break

4:05 PM Invited

Oxygen Enhanced Crack Growth in Nickel-Based P/M Superalloys: *Robert P. Wei*[1]; [1]Lehigh University, Dept. of Mech. Eng. and Mech., 7 Asa Dr., Bethlehem, PA 18015 USA

As a part of a study to elucidate the role of niobium on crack growth in oxygen at high temperatures, three powder metallurgy (P/M) alloys, with nominal composition similar to alloy IN-100, but with 0, 2.5 and

5 wt. pct. niobium, were investigated. These alloys are γ strengthen and were designed to suppress the formation of γ' precipitates. The volume fraction of precipitates in the alloys is comparable at about 53 pct. The alloys were tested in high-purity oxygen and argon, under sustained-loading, at 873, 923 and 973 K. Companion microstructural and surface chemistry studies were also conducted. In this paper, the data on the kinetics of crack growth will be summarized and compared against those for Inconel 718. The mechanisms for crack growth and the role of niobium and of other elements will be discussed in terms of the ensemble of results.

4:30 PM

Temperature Evolution during High-Cycle Fatigue in ULTIMET® Superalloys: *L. Jiang*[1]; P. K. Liaw[1]; C. R. Brooks[1]; H. Wang[2]; D. L. Klarstrom[3]; [1]University of Tennessee, Dept. of Matls. Sci. and Eng., 427-B Dougherty Eng. Bldg., Knoxville, TN 37996-2200 USA; [2]Oak Ridge National Laboratory, 1 Bethel Valley Rd., Oak Ridge, TN 37831-6064 USA; [3]Hayes International Inc., 1020 W. Park Ave., P.O. Box 9013, Kokomo, IN 46904-9013 USA

The infrared (IR) thermography, as a nondestructive technique, was used to investigate the fatigue damage of ULTIMET® alloy, a cobalt-based superalloy. The cumulative fatigue damaging process was characterized by the temperature changes during high-cycle fatigue. A noncontact, high-speed, and high-resolution IR thermoimaging system was capable of monitoring the temperature oscillation corresponding to the change of the mechanical state during high-cycle fatigue testing. A thermodynamic model is presented for predicting the thermal-mechanical response. The predicted temperature response was found to be in good agreement with the experimental results.

4:50 PM

The Effects of Heat Treatment on Time-Dependent Fatigue Crack Propagation in a Low Thermal Expansion Superalloy INCONEL 783: *Longzhou Ma*[1]; Keh-Minn Chang[1]; Sarwan K. Mannan[2]; [1]West Virginia University, Mech. and Aerospace Eng. Dept., P.O. Box 6106, Eng. Sci. Bldg., Morgantown, WV 26506-6106 USA; [2]Special Metals Corporation, 3200 Riverside Dr., Huntington, WV 25705 USA

Recently developed alloy 783 (nominal composition of Ni-34Co-26Fe-5.4Al-3Nb-3Cr) is precipitation strengthened by Ni_3Al-type β and NiAl-type γ phases. Due to its low coefficient of thermal expansion, high strength, and good oxidation resistance, alloy 783 is used for casings and bolting applications in gas turbines. Commercial alloy 783 plate was rolled in the laboratory to 50% reduction at 870°C. A part of the plate was direct aged and the other part was annealed at 1121°C and aged. This was followed by fatigue crack propagation of the aged materials at 300°C, 450°C, 600°C, and at room temperature. Tests were carried out at 10 Hz and 1/3 Hz using sinusoidal loading and also under a 100-second hold time using trapezoidal waveform. Interestingly, the crack growth rates of direct aged and annealed plus aged materials were not significantly different.

5:10 PM

Effects of Heat Treatments and Thermomechanical Processing on the Beta and Gamma Phases in Inconel 783 Alloy: *Mohindar S. Seehra*[1]; A. Manivannan[1]; Codrin Cionca[1]; L. Ma[1]; Keh-Minn Chang[1]; [1]West Virginia University, Morgantown, WV 26506 USA

Inconel 783 is a low CTE alloy in which the role of β phase is important but not well understood. Here, changes in the β and γ phases in alloy 783 upon heat treatments and thermomechanical processing (TMP) are studied using x-ray diffraction (XRD), thermogravimetric analysis (TGA) in a magnetic field and microstructural observations. TMP included: HR0 (hot rolled to ¾ inch at 2000°F); HR1 (HR0 rolled 50% at 1600°F); HR2 (HR0 rolled 50% at 1850°F) and HR3 (HR0 rolled 50% at 2100°F). Heat treatments included normal treatment (NT) and direct aging (DA). HR0DA contains only the -phase and no magnetic transition (T_c) above 25°C. Samples HR1DA, HR2DA and HR3DA have β and γ phases and two T_c's near 390°C and 490°C. For HR1NT and HR2NT, β phase is weak and T_c at 390°C is lowered to 352°C. These results will be discussed relative to thermodynamic calculations on phase formation and phase chemistry.

Aluminum Reduction Technology: Cell Development/Operation

Sponsored by: Light Metals Division, Aluminum Committee
Program Organizers: John Chen, University of Auckland, Department of Chemical & Materials Engineering, Auckland, New Zealand; Georges J. Kipouros, Dalhousie University, Department of Mining and Metallurgical Engineering, Halifax, NS B3J2X4 Canada

Monday PM — Room: Sewanee
March 13, 2000 — Location: Opryland Convention Center

Session Chair: Alton Tabereaux, Reynolds Metals Company, Corp. Rsrch. and Dev., Muscle Shoals, AL 35661-1625 USA

2:00 PM Invited

Development of High Amperage Prebaked Cells in China: S. Z. Feng[2]; Z. X. Leng[2]; *Yiren Gan*[1] [1]Zhengzhou Light Metal Research Institute, Shangjie, Zhengzhou China; [2]Guizhou Aluminium Plant, Guiyang, Guizhou China

Aluminium production capacity in China is over 2.5 million tonnes/annum, but the main type of pots is Soderberg pot. In order to change the backward situation, a development program for high amperage point-fed prebaked pot has been carried out since the latter part of the 1970's. A laboratory has been set up to carry out basic research work on electro-magnetic-hydrodynamics, thermal balance and other parameters in aluminium pots. It includes modeling tests, measuring methods in laboratory and industrial pots, development of mathematical modeling and calculation program. After testing and verifying the results in industrial pots, new types of 186kA and 280kA pots have been developed and tested successfully in pilot plants. Based on the test results, 2 lines of 186kA pots have been set up and are in production, another 2 lines are in construction and 2 lines of 280kA pots are planned for construction. This technology will be used in new aluminium plants in China. A 320kA testing line will be put into production soon.

2:30 PM

Danjiangkou-A Step Forward: *Hugh McLaughlin*[1]; Guo Xing[2]; [1]VAW Aluminium-Technologie GmbH, P.O. Box 101554, Neuss D-41415 Germany; [2]Danjiangkou Aluminum Industry Company, Hubei Province, China

VAW's former Toeging 1 smelter in Germany has been purchased by the Danjiangkou Aluminium Industry Company, Ltd. and successfully relocated to China. The startup of these facilities during 1999, supported by VAW-ATG, has upgraded and expanded the existing Soderberg plant. Today it is one centered around a 100 pot, highly efficient, end to end prebake, complete with a modern computer control system. This low cost modular design was producing aluminum only 14 months after start of construction. This 114.5 kA potline operated consistently at over 94% current efficiency with a power consumption of 13.4 kWh/kg during its former life. Its sale to China, due to power constraints in Germany, and its efficient reassembly and startup reflect favorably on the design and operational stability of this cell. The pots are equipped with center hoppers for alumina, aluminium fluoride, and crushed bath. Crust breakers and point feeders are incorporated in the hoppers. The VAW technology featuring pot design and hardware as well as the ELAS pot control system bring an era of new life to the aluminium smelting industry in central China. This paper presents some details around this project and emphasises the extreme interest within China to upgrade their aluminium smelting facilities.

2:55 PM

Satisfying Financial Institutions for Major Capital Projects: *Jan Heintzen*[2]; *Robert Paul Harrison*[1]; [1]Hatch, Light Metals Grp., 5 Place Ville-Marie, #200, Montreal, Quebec H3Z3R9 Canada; [2]Beddows

& Company, Aluminum Projects, 5 Place Ville-Marie, Montreal, Quebec H3B2G2 Canada

Major capital investments in the aluminum sector require significant financing, often in the hundreds of millions of dollars. Lenders are understandably conservative about transactions of this magnitude, and impose not only contractual and financial obligations but technical ones as well. A project must be technologically sound, properly staffed and managed, and environmentally acceptable-to the satisfaction of the banks-before they will disburse the required capital. With permission from the Billiton Group, two recent examples are presented to illustrate these concepts: the construction of the Hillside smelter in South Africa, and the acquisition of Worsley Alumina in Australia.

3:20 PM

The Effect of Anode Spike Formation on Operational Performance: *Bernd Rolofs*[1]; Neal Wai-Poi[1]; [1]Hoogovens Aluminium Huttenwerk GmbH, Postfach 101154, Voerde D46549 Germany

Since the start-up of the Voerde smelter in 1970, several upgrades and retro-fits of the existing P69 technology have been completed. These include, the introduction of bigger anodes and the implementation of Celtrol2 computer process control system. These and other modifications enabled the Voerde smelter to make significant improvements in cell performance and operations, resulting in e.g.94+% current efficiency and an average cell life of 2600 days. However, since the conversion from wet to dry scrubbing in 1992, the smelter has experienced a persistent problem with carbon dust levels. As a consequence, the anode spike frequency has increased significantly. The spiking has had a negative impact on current efficiency, typically a 1.6% loss and resulted in a greater variation in operational parameters. Therefore, several trials have been conducted to investigate the origin of the carbon dust, the impact on cell operations and the influence of operating practices on spiking.

3:45 PM Break

3:55 PM

Aspects of Field Studies on Hall-Heroult Cells: *Nolan E. Richards*[1]; [1]Richards Consulting, 117 Kingswood Dr., Florence, AL 35630 USA

Whenever a meaningful database for the performance of a cell representative of a potline is needed, a comprehensive characterization of such a cell should be considered. Such a characterization is even more desirable when modifications to any aspect of the cell, e.g., bath chemistry, anode area, line current, thermal insulation, protocol for alumina additions are planned. Comprehensive field studies are also important in ensuring that the performance of a cell representative of a greenfield potline falls within the prescribed targets. Recommendations are given for an array of in situ field measurements and methods for conducting them. Typical results and sensitivities are presented. Examples of the data obtained from a selection of cells are shown and discussion offered of the synergism and interpretation of some results.

4:20 PM

Advanced Solid Bath Transport at DUBAL: *W. A.R. Al-Sayed*[1]; J. Ifju[2]; I. Del Porto[2]; M. Moni[2]; [1]Dubai Aluminium Company, P.O. Box 3627, Dubai United Arab Emirates; [2]Techmo Car Spa, Via R. Colpi, Limena(PD) 35100 Italy

Recycling the materials extracted from the cells and removed temporarily from the smelting process due to periodic operation of the prebaked anodes is compulsory in order to maintain high efficiency and performance of the primary aluminium smelting. Utilization of the solid bath requires a series of operations including its handling, processing and transport which has to be fulfilled in a safest way and lowest possible losses. A tailor-made and specially designed vehicle has been developed for the Dubai Aluminium Company Ltd. in close cooperation with the operation experts aimed at efficient handling, fast and safe transport taking into account environment protection and good working conditions for the operators. This paper describes the work done and economical effect in relation to the use of vehicles with innovative concept of design named Easy Truck.

4:45 PM

Design of Shunt Rheostat for Coke-Bed Preheating of Aluminium Reduction Cells: S. A. Mohamed[1]; *F. M. Ahmed*[1]; [1]Aluminium Company of Egypt, Rsrch. and Dev., Naga-Hammadi, Egypt

Coke-bed preheating is one of the most popular methods to preheat aluminium reduction cells. The preheating by this method can be achieved with partial or full line current. To achieve preheating without full line current, shunt resistance is employed. The design procedure of shunt resistance includes, selection of material, collection of preheating and cell design data, thermoelectric calculations in addition to the assembly and detail drawings. In this paper, the steps taken to design two different groups of shunt resistance fox preheating of 200kA end to end, prebaked anode cell is explained. The results of applying the different designs in preheating of aluminium cells are discussed.

5:10 PM

Reduction Cell Technology Development at DUBAL through 20 Years: A. J.M. Kalban[1]; *Y. A.M. Al Farsi*[1]; A. S.S. Binbrek[1]; [1]Dubai Aluminium Company Limited, P.O. Box 3627, Dubai United Arab Emirates

The Dubai Aluminium Company Limited (DUBAL) smelter commenced operations in 1979 with 3 potlines comprising 360 prebaked cells at 150 kA and producing 135,000 tonnes of aluminium annually. By 1990, a series of continuous, innovative improvements to the cell components and operational practices radically transformed the original cell technology to operate at 180 kA. An expansion of 139 cells in Potline 4 resulted in a total of 499 cells producing ~ 250,000 tonnes aluminium annually. By 1996, having developed, jointly with Comalco, and tested five prototype CD-200 reduction cells at 200 kA, DUBAL installed 240 cells in Potline 5. Total cells thereby increased to 739 and annual production to 375,000 tonnes. In 1999, another 240 CD200 cells were commissioned in Potline 6 increasing the cell population to 984 cells and annual production to 536,000 tonnes of high quality aluminium whilst generating 1400 MW power through natural gas-fueled turbines. This paper tracks 20 years of DUBAL's continuous advancement in reduction cell technology, both in terms of improvements and development.

Automotive Alloys 2000: Fundamental

Sponsored by: Light Metals Division, Aluminum Committee
Program Organizer: Subodh K. Das, University of Kentucky, College of Engineering, Center for Aluminum Technology, Lexington, KY 40506-0043 USA

Monday PM — Room: Knoxville A
March 13, 2000 — Location: Opryland Convention Center

Session Chair: Subodh K. Das, University of Kentucky, College of Eng., Lexington, KY 40232 USA

2:00 PM

Precipitation of Iron Containing Phases in 319 Type Alloys during Solidification: *Jacob W. Zindel*[1]; Larry A. Godlewski[1]; William T. Donlon[1]; [1]Ford Motor Company, Ford Rsch. Lab., P.O. Box 2053, Dearborn, MI 48121 USA

Al-Si-Cu-Mg alloys, commonly referred to as 319, are widely used in the production of cast aluminum automobile powertrain components. Secondary alloys such as these contain iron as an impurity as a result of contamination in the recycling stream. During solidification, iron containing intermetallic compounds form which have been attributed to increasing the propensity for microporosity formation, decreasing ductility, and reducing fatigue strength of castings. In an effort to understand how to control the formation of these phases, work has been conducted to characterize their nucleation and growth. This study consisted of interrupting the solidification of 319 alloy samples with different Fe concentrations by quenching them into an iced-brine bath. Samples with 0.40, 0.65, and 0.95 wt.% Fe were quenched at

various solid fractions to determine when the various iron compounds precipitate. Typically, two Fe-containing phases are observed in these alloys, a cubic phase, alpha, with the approximate stoichiometry of Al15(Fe,Mn)3Si2 and a monoclinic phase, beta, with the approximate stoichiometry of Al5FeSi. In the 0.4 wt.% Fe alloy, alpha appeared to have precipitated after the nucleation of the Al-Si eutectic. No other iron compounds were observed in this alloy. In the 0.65 and 0.95 wt.% Fe alloys, a tetragonal phase, delta (Al4Si2Fe), was observed to precipitate near the liquidus followed by alpha and beta precipitation at a temperature above the Al-Si eutectic reaction. The temperature of the thermal arrest due to Fe compound precipitation increased with increasing Fe concentration.

2:25 PM

Improving Stress Corrosion Cracking in Al-Mg Alloys: *John S. Vetrano*[1]; M. J. Danielson[1]; D. R. Baer[1]; R. H. Jones[1]; [1]Pacific Northwest National Laboratory, MSIN P8-16, P.O. Box 999, Richland, WA 99352 USA

The use of Al-Mg alloys with Mg levels of greater than 3.5 wt.% for automotive structural components is hampered by their susceptibility to stress corrosion cracking (SCC) in salt water. Segregation of Mg to grain boundaries causing precipitation of the Al3Mg2 (b) phase during low-temperature thermal exposure (sensitization) has been shown to be the primary cause of SCC in these alloys. We have utilized alloying additions and tailored heat treatments to lessen the SCC susceptibility in Al alloys containing up to 7% Mg following sensitization heat treatments at 175°C. Alloying additions studied include Zn, Mn and Sc, at levels allowing the study of solid solution and precipitate effects. Both Mn additions and a slower cooling rate from the initial annealing prior to sensitization treatment reduced the SCC susceptibility as measured by the ASTM G-67 weight loss tests. Allowing the samples to cool in the furnace reduced the SCC susceptibility compared to those samples that were water quenched after annealing. Additionally, the addition of 0.09 wt.% Cu reduced the SCC susceptibility although evaluation is still in progress. The effects of alloying additions and thermal treatment on the SCC behavior of Al-7 wt.% Mg alloys are thought to be due to a change in grain boundary b phase precipitation. Work supported by the Materials Division, Office of Basic Energy Sciences, U.S. Department of Energy under Contract DE-AC06-76RLO 1830.

2:50 PM

The Precipitation Sequence in 6111 Aluminum Alloy: Weifang Miao[1]; *David E. Laughlin*[1]; [1]Carnegie Mellon University, Dept. of Matls. Sci. and Eng., 5000 Forbes Ave., Pittsburgh, PA 15213 USA

The hardening of 6111 aluminum alloy is realized through the precipitation of various metastable precipitates, therefore a more in depth understanding of the precipitation sequence is very important to achieve the full strengthening potential of the alloy. While the focus of previous investigations of the precipitation hardening behavior in Al alloy 6111 has been on the aging response, many details of the precipitation process remain unclear. In this paper, the precipitation sequence in Cu-containing Al alloy 6111 has been studied by means of differential scanning calorimetry and transmission electron microscopy. It was found that in contrast to the precipitation sequence in Al-Mg-Si alloys, which is usually GP zones—needle-like $_{\beta}$"—rod-like $_{\beta}$'—$_{\beta}$ platelets, the precipitation sequence in the 6111 alloy is believed to be: GP zones—needle-like $_{\beta}$"—lath-like Q'—Q. Financial support from Ford Motor Company is gratefully acknowledged.

3:10 PM

Effect of Different Natural Aging Times on the Precipitation Behaviour of AA6111: *Shahrzad Esmaeili*[1]; Warren James Poole[1]; David J. Lloyd[2]; [1]University of British Columbia, Dept. of Metals and Matls. Eng., 309-6350 Stores Rd., Vancouver, BC V6T1Z4 Canada; [2]Alcan International, Kingston Rsch. and Dev. Ctr., P.O. Box 8400, Kingston, ON K7L5L9 Canada

It has been shown that natural aging after solution treatment negatively affects the subsequent artificial aging response for 6000 series aluminum alloys. In this work, the effect of different natural aging times has been examined for the automotive alloy AA6111. The level of natural aging time was varied from 0 to 4 months and was then followed by artificially aging at 180°C. The changes in microstructure were characterized using tensile tests, electrical resistivity measurements, differential scanning calorimetry (DSC) and transmission electron microscopy (TEM). Electrical resistivity measurements were found to be very sensitive to the heat treatment procedure and can be used to provide information on the formation of solute clusters and their subsequent dissolution during artificial aging. It was also found useful to conduct DSC traces after different levels of artificial aging to follow the sequence and kinetics of precipitation. The results from this work confirmed that natural aging significantly reduced the strength at short artificial aging times. As the level of natural aging was increased, this effect was increased. However, for natural aging times greater than approximately 7 days, a further increase in natural aging time had a much smaller effect. It is thought that the formation of solute clusters during natural aging reduces the solute available for precipitation at higher temperatures. It appears that dissolution of clusters in order to free up solute for precipitation is the rate controlling process during the initial stages of artificial aging.

3:30 PM Break

3:50 PM

The High-Cycle Fatigue and Fracture Response of Al-Cu-Mg Alloy 2524: *T. S. Srivatsan*[1]; D. Kolar[1]; P. Magnusen[2]; [1]The University of Akron, Dept. of Mech. Eng., Akron, OH 44325-3903 USA; [2]Aluminum Company of America, Alcoa Tech. Ctr., 100 Technical Dr., Alcoa Center, PA 15069 USA

The design of structural components for the newer generation of civilian and military aircraft demands satisfactory performance from the material under conditions of cyclic stress amplitude and strain amplitude control, and an extended service life. In this connection, a study has been made to understand the influence of test temperature on cyclic stress amplitude response characteristics and fatigue life of aluminum alloy 2524. Test specimens of the alloy were cyclically deformed over a range of stress amplitudes at both ambient and elevated temperatures. In this presentation, the stress response characteristics and resultant fatigue properties of the alloy will be highlighted in light of the competing and mutually interactive influences of cyclic stress amplitude, intrinsic microstructural effects, matrix deformation characteristics and final fracture behavior. Research supported by State of Ohio: Board of Regents (Columbus, OH, USA), and The University of Akron (Akron, OH, USA).

4:10 PM

Fatigue Performance of Mechanically Surface Treated Aluminum and Magnesium Alloys: *Lothar Wagner*[1]; Matthias Hilpert[1]; [1]Technical University of Brandenburg at Cottbus, Chair of Matls. Tech. and Physical Metallu., P.O. Box 101344, Cottbus D-03013 Germany

The effect of shot peening and roller-burnishing on the HCF behavior of two widely used automotive light-weight alloys (6061 Al and the magnesium alloy AZ 31) was studied. For shot peening and roller-burnishing, the main process parameters Almen intensity and rolling force, respectively were widely varied to optimize fatigue performance. The electrolytically polished condition served as a reference. Fatigue tests were performed in rotating beam loading (R=-1) in air and in 3.5% aqueous NaCl solution at frequencies of about 60 Hz. It was found that the response of the magnesium alloy to shot peening depended strongly on Almen intensity, i.e., pronounced lifetime improvements were observed only in a range of very low Almen intensity. Higher intensities led to marked overpeening effects. In contrast, the aluminum alloy showed no loss in lifetime with increasing Almen intensity. Since both alloys responded with a similar lifetime improvement to increasing rolling forces in roller-burnishing (which generally leads to a smooth surface finish) it is argued that the shot peening-induced high surface roughness and microcracks are the main reason for the marked sensitivity of the magnesium alloy to Almen intensity in shot peening.

4:30 PM

Comparison of Microstructures between the As Cast and Rapidly Solidified A 390 Alloy: *E. G. Baburaj*[1]; R. Fielding[1]; K. Prisbrey[2]; J. Hill[3]; R. Oswald[3]; F. H. (Sam) Froes[1]; [1]University of Idaho, Instit. for Matls. and Adv. Processes, 321 Mines Bldg., Moscow, ID 83844-3026 USA; [2]University of Idaho, Dept. of Metallu. and Mining Eng., Moscow, ID 83844-3024 USA; [3]LA Aluminum Casting, W. 1905 Miles Ave., Hyden Lake, ID 83835 USA

The hyper eutectic Al-Si base alloy A 390 (Al-17.5Si-4.5Cu-0.5Fe-0.1Mn-0.55Mg-0.1Zn) is a better alternative to the widely used A356 (Al-7Si-0.2Cu-0.2Fe-0.1Mn-0.3-Mg0.1Zn-0.2Ti) due to its superior properties which include good liquid alloy fluidity, small solidification range, high strength and rigidity, good thermal conductivity, low thermal expansion coefficient and good resistance to abrasion, wear and corrosion. However A390 finds limited use due to poor ductility of the cast structure which usually consists of a eutectic matrix with a distribution of blocky primary Si particles. Modification of the alloy, through addition of P, Na and Sr, is known to reduce the primary Si particle size and thereby improve the ductility. Application of rapid solidification processing of the alloy can further reduce the particle size of silicon. The present paper is a comparison of the effects of trace elements and cooling rate on the microstructure of the alloy.

4:50 PM

The Effect of Porosity on the Fatigue Properties in a Cast 319 Al Alloy: *James M. Boileau*[1]; John E. Allison[1]; [1]Ford Motor Company, Scientific Rsch. Labs., MD 3182 SRL, P.O. Box 2053, Dearborn, MI 48121-2053 USA

As the automotive industry increases its use of cast aluminum components, the need for more detailed information relating the effect of casting practice on fatigue behavior also increases. One of the key factors influencing the fatigue of cast aluminum is porosity. Therefore, a study characterizing the influence of solidification time on the microstructure and fatigue properties in a cast 319 Al alloy was conducted. Multiple fatigue tests were conducted on a cast 319 Al alloy (T6 and T7 heat-treatments) at selected stress levels so that valid statistical comparisons could be made. Extensive metallographic and fractographic characterization was performed to understand the influence of pore size and distribution on fatigue life. In general, microporosity was associated with all of the fatigue failures and was located at or near the specimen surface. Also, as solidification time increased, the average initiating pore diameter increased and the number of samples having multiple initiating sites tended to increase. Multiple initiating sites were observed in several samples and were observed to have an effect on the fatigue. Quantitative measurements of microporosity found that conventional metallographic techniques substantially underreport the maximum pore size present in the W319 alloy.

5:10 PM

Age Softening of AA5182 Alloy: *Jian Chen*[1]; James G. Morris[1]; [1]University of Kentucky, Chem. and Matls. Eng. Dept., Anderson Hall 177, Lexington, KY 40503 USA

The age softening phenomenon of AA5182 alloy was studied. The effect of different degrees of cold rolling, aging temperature, homogenisation temperature on the age softening behavior were measured. It was found that no observable changes in crystallographic texture, grain size, particle size and distribution and even in dislocation structure occur during the age softening process, but the electricity resistivity decreases continuously. The age softening process is a thermally activated and it accelerates with increasing aging temperature. The activation energy of the age softening process was measured. The mechanism to cause this phenomenon is discussed.

Cast Shop Technology: Modeling Solidification and Flow

Sponsored by: Light Metals Division, Aluminum Committee
Program Organizers: Paul Crepeau, General Motors Corporation, GM Powertrain Group, Pontiac, MI 48340-2920 USA; James N. O'Donnell, Commonwealth Aluminum Corporation, Department of Engineering, Louisville, KY 40202-2823 USA

Monday PM — Room: Mississippi
March 13, 2000 — Location: Opryland Convention Center

Session Chair: Yogesh Sahai, Ohio State University, Dept. of Matls. Sci. and Eng., Columbus, OH 43210 USA

2:00 PM Opening Remarks

2:05 PM

3-D Modeling of Fluid Flow and Heat Transfer during the DC Casting Process-Influence of Flow Modeling Approach: *Gerd Ulrich Gruen*[1]; Dag Mortensen[2]; Andreas Buchholz[3]; [1]VAW Aluminium AG, Rsch. and Dev., Georg-von-Boeselager-Strasse 25, Bonn D-53117 Germany; [2]Institute for Energy Technology, Process Simulation Dept., P.O. Box 40, Kjeller N-2007 Norway; [3]Hoogovens Research & Development, Computational Fluid Dynamics, P.O. Box 10000, IJmuiden 1970 CA The Netherlands

The improvement of the DC casting of aluminum rolling and extrusion ingots is an ongoing process. Besides implementation of optimized mold systems and automated control of the main process parameters casting temperature, casting speed, metal level, and water cooling, the optimization of liquid metal distribution systems is an actual matter of research. Various numerical models of the coupled fluid flow and heat transfer phenomena dominating the DC casting process have been developed and used for understanding the complex interactions between liquid transport and temperature evolution in the solidifying ingot. Although they are based on the same set of equations some differences exist concerning the implementation of the flow phenomena. In order to evaluate the influence of the chosen fluid flow model (laminar, turbulent) on the resulting velocity and temperature distribution, three different 3-dimensional implementations used in the aluminum industry (based on the software ALSIM, FIDAP, PHOENICS/CFX) are compared by means of a set of well defined reference cases. The resulting temperatures and flow patterns of the three models are discussed in dependence of modified material properties, boundary and geometrical conditions and implemented flow model parameters. In addition, the results are qualitatively compared with temperature measurements in the liquid pool during an experimental trial program.

2:30 PM

Effect of Mushy Zone Mechanical Properties on the Calculated Stresses and Deformations during the Casting of an Aluminum Alloy Ingot: *Alvaro Giron*[1]; Men Glenn Chu[1]; Ho Yu[1]; [1]Alcoa Inc., Alcoa Tech. Ctr., 100 Tech. Dr., Alcoa Center, PA 15069 USA

An improved constitutive model which describes the mechanical behavior within the freezing range of an aluminum alloy has been used to estimate the stresses and deformations during the early stages of the DC casting process. Comparison is made with the stresses and deformations calculated with a similar constitutive model that extrapolates property data measured at lower temperatures.

2:55 PM

Determination of Boundary Conditions Using Inverse Stationary Methods: *Jean Marie Drezet*[1]; Gerd-Ulrich Gruen[2]; Marco Gremaud[3]; [1]Laboratoire de Metallurgie Physique Calcom SA, Ecole Polytechnique Federale de Lausanne, MXG Ecublens, Lausanne CH-1015 Switzerland; [2]VAW Research and Development, VAW Aluminum

AG, P.O. Box 2468, Bonn D-53014 Germany; [3]Calcom SA Parc Scientifique, Ecole Polytechnique Federale, De Lausanne PSE, Lausanne CH-1015 Switzerland

The direct chill (DC) casting process is widely used in the aluminium industry to produce rolling sheet ingots and extrusion billets. In both processes, the metal is cooled down firstly by contact with the mould (primary cooling) until an air gap forms and reduces the heat transfer to almost zero, and secondly by application of a water jet on the ingot surface (secondary cooling). In order to quantify the cooling conditions undergone by an ingot during DC casting, temperatures were measured by thermocouples immersed in the liquid pool and then entrapped by the solid. In run conditions of casting, the thermal field is stationary in a reference attached to the mould. Therefore, the measured temperature histories were converted into temperature profiles and used in the inverse method described by Rappaz et al. and adapted to stationary temperature conditions. This allowed to deduce in a first the temperature dependent thermal conductivity of the alloy, and to determine in a second step the highly non uniform distribution of the thermal heat flux extracted at the lateral surface of the ingot and corresponding to the primary and secondary cooling.

3:20 PM

Modeling of Solidification of Al Alloys in a Laboratory Scale DC-Simulator: *Xiaohong Yang*[1]; [1]University of Quebec at Chicoutimi, Dept. of Appl. Sci., 555 Blvd. De l'Universite, Chicoutimi, Quebec G7H2B1 Canada

A mathematical model has been developed in order to study the influence of natural convection on the solidification of aluminium alloys during direct-chill (DC) casting. The computer model simulates heat transfer, fluid flow, solid transport and microstructure evolution during solidification in a laboratory scale DC-simulator using the volume averaging method. It deals with both macroscopic and microscopic aspects of solidification. Both equiaxed structure and columnar structure, as well as the columnar-equiaxed transition, are incorporated in the model. The simulated results fitted well with the experimental data, and it was shown that natural convection has significant effects on the temperature field.

3:45 PM Break

3:50 PM

Microporosity Prediction in Aluminum Alloy Castings: *Adrian S. Sabau*[1]; *Srinath Viswanathan*[1]; [1]Oak Ridge National Laboratory, Metals and Ceramics, Bldg. 4508, MS 6083, Oak Ridge, TN 37831 USA

As part of a program to develop models for the prediction of microporosity in cast lightweight automotive structural parts, a comprehensive model that takes into account solidification, shrinkage-driven interdendritic fluid flow, hydrogen precipitation, and porosity evolution has been developed for the prediction of microporosity fraction. Experimentally determined values of liquid metal permeability in the mushy zone were used to calculate pressure distributions in solidifying castings. The pressure distribution in a solidifying casting, coupled with a microporosity criterion involving the local hydrogen concentration and the effect of surface tension, is used to predict microporosity distributions in aluminum alloy castings. The results are compared with experimentally measured microporosity distributions in A356 aluminum alloy test castings.

4:15 PM

A 2D Cellular Automaton-Finite Difference (CAFD) Model of the Solidification of Aluminium-Rich Al-Cu-Si Alloys: *David John Jarvis*[1]; *John Anthony Spittle*[1]; Stephen Graham Brown[1]; [1]University of Wales, Matls. Eng. Dept., Singleton Park, Swansea, Wales SA28PP United Kingdom

A 2D cellular automaton-finite difference (CAFD) model has been developed for simulating the solidification transformations in ternary aluminium-rich Al-Cu-Si alloys. A novel feature of the model is that initial primary phase solidification occurs in a dendritic fashion, either columnar or equiaxed. A combined curvature/surface energy anisotropy routine ensures that dendrite arm growth occurs orthogonally. The model overcomes many of the limitations of traditional 1D plate numerical models by allowing solidification and solute redistribution to occur within a naturally evolving microstructure. In addition, the model allows for diffusional solute mixing in both the solid and liquid phases during the primary phase and monovariant Al-Si eutectic stage of freezing. This paper demonstrates the predicted influence of cooling rate on the proportions of primary phase, binary eutectic and ternary eutectic under non-equilibrium freezing conditions for a range of alloy compositions.

4:40 PM

Microstructure Prediction in A356 Alloy Castings: *Qingyou Han*[1]; *Srinath Viswanathan*[1]; [1]Oak Ridge National Laboratory, Metals and Ceramics, Bldg. 4508, MS 6083, Oak Ridge, TN 37831 USA

As part of a program to develop advanced tools for the design and optimization of structural A356 aluminum alloy castings, models have been developed and used for predicting phase fractions and microstructural length scales. The models predict phase evolution during solidification and the final length scales after solidification. These length scales are the primary dendrite size, secondary dendrite arm spacing, and cell spacing for the primary aluminum phase and the particle/rod size for the silicon phase. Mechanisms governing the growth of these phases are considered in the models. The predictions are compared with independent measurements by other researchers and with data from the literature. The results of the models are presented in the form of analytical equations for each of the length scales. The simple form of the equations allow them to be used in the post processing step of commercial solidification codes for the prediction of microstructure in shape castings.

5:05 PM

Enthalpy Variations and Latent Heat Evolution during Solidification of Lead-Tin Alloys: Sergio Fabian Gueijman[1]; Alicia Esther Ares[1]; *Carlos Enrique Schvezov*[1]; [1]University of Misiones, Faculty of Sci., Azara 1552, Posadas, Misiones 3300 Argentina

In order to achieve improved predictions in a solidification process using mathematical modeling, it is necessary to couple the solidification modeling with an accurate thermodynamic model. In the present report, several thermodynamics aspects related to solidification of Lead-Tin alloys are considered. Such aspects are; the solidification path, the solid fraction vs. temperature, and the enthalpy and the latent heat evolution. A thermodynamic model including the above phenomena is developed and the values of the associated parameters are calculated, particularly the enthalpy of the solid and liquid phases of the alloys in the mushy zone, as a function of temperature and alloy concentration. From the calculated enthalpies, the latent heat released during solidification, which is a key input parameter in any solidification model, can be readily obtained. The total integrated heat released for complete solidification of Lead-Tin alloys calculated with the present model are in good agreement.

Cyclic Deformation and Fatigue of Materials; A Symposium in Honor of Professor Campbell Laird: Cyclic Deformation and Mechanism (I)

Sponsored by: ASM International: Materials Science Critical Technology Sector, Structural Materials Division, Jt. Mechanical Behavior of Materials

Program Organizers: Zhirui Wang, University of Toronto, Department of Metals and Materials Science, Toronto, Ontario, Canada; Charles McMahon, University of Pennsylvania, Department of Materials Science and Engineering, Philadelphia, PA 19104 USA; Pedro D. Peralta, Arizona State University, Department of Mechanical and Aerospace Engineering, Tempe, AZ 85287-6106 USA; J. K. Shang, University of Illinois, Department of Materials Science and Engineering, Urbana, IL 61801 USA

Monday PM — Room: Canal A
March 13, 2000 — Location: Opryland Convention Center

Session Chairs: P. Lukas, Institute of Physics of Materials, Brno Czech Republic; Z. Wang, University of Toronto, Dept. of Met. & Matls. Sci., Toronto, Ontario, Canada

2:00 PM

Effect of Loading History on Cyclic Stress-Strain Response and Cyclic Creep: *L. Kunz*[1]; P. Lukas[1]; B. Weiss[2]; D. Melisova[2]; [1]Institute of Physics of Materials, ASCR, Brno Czech Republic; [2]University of Vienna, Instit. of Matl. Physics, Vienna, Austria

Cyclic plasticity of metals depends on loading history. The cyclic hardening/softening, steady-state behaviour, cyclic strain localisation, fatigue limit and fatigue lifetime are influenced by preceding deformation, both cyclic and monotonic. A cyclic mechanical equation of state, relating the saturation stress-amplitude with the saturation-strain amplitude, is generally not applicable. The changes of microstructure due both to the monotonic and cyclic strain are considered to be the main reason for these effects. The aim of this contribution is to summarise the effect of the loading history on the cyclic stress-strain response of Cu and Ni and to contribute to the completion of the partial understanding of the influence of the loading history represented by different ramp loading and pre-strain on the cyclic plasticity and cyclic creep. It will be shown that the cyclic stress-strain response (cyclic stress-strain curves), dislocation microstructure and the strain localisation both in single and polycrystals are strongly influenced by the start-up procedure (ramp loading) and pre-strain. Both the ramp loading (its length and the details of the load increase sequence) and the pre-strain in the first loading cycle (implicitly introduced in tests with the mean stress) affects the cyclic creep behaviour, plastic strain amplitude and the number of cycles to fracture elapsed at full stress amplitude. The saturated plastic strain amplitude has been found to be related to the cyclic creep strain in saturation. This indicates that the description of the cyclic plasticity entirely in terms of the plastic strain amplitude is insufficient and additional data on the cyclic creep (monotonic strain) are inevitable.

2:25 PM

Cyclic Plastic Deformation Behaviour of Ni Single Crystals Oriented for Single Slip as a Function of Hydrogen Content: *Thierry Magnin*[1]; C. Bosch[1]; K. Wolski[1]; [1]Ecole des Mines de Saint-Etienne, Ctr. SMS URA CNRS 1884, 158 Cours Fauriel, St Etienne, Cedex02 42023 France

Ni single crystals oriented for single slip exhibit as Cu crystals a well defined stress-strain curve at room temperature corresponding to PSB formation in a given plastic strain range. The aim of this paper is to study the influence of hydrogen on the cyclic plastic behaviour of such crystals, in comparison with pure crystals. This is of particular interest in two cases: when hydrogen enters the materials during the fatigue test (corrosion fatigue under cathodic charging) and when hydrogen-precharge has been made before cycling. It is known that hydrogen decrease the cross slip ability in fcc Ni crystals at room temperature. However, the influence of cross slip on PSB formation and evolution is known to be quite important. Thus the influence of hydrogen on the PSB formation and the corresponding cyclic plastic behaviour is analysed on pure Ni single crystals in two experimental conditions: during corrosion fatigue in a 0.5N H_2SO_4 solution at applied cathodic potential and during fatigue after hydrogen precharging. A particular attention is paid on the effect of hydrogen on cyclic softening. TEM analyses emphasize such influence. Mechanical consequences are then detailed.

2:50 PM

Mean Stress Effect on Cyclic Plastic Deformation of Industrial Pure Iron: *Hai Ni*[1]; Zhirui Wang[1]; [1]University of Toronto, Dept. of Metallu. and Matls. Sci., Toronto, Ontario M5S3E4 Canada

It has been reported recently that sagging behavior in spring steels is a direct result of asymmetrical cyclic loading. Although previous work showed that cyclic creep and cyclic softening are the two main causes for sagging in mechanical springs, the mechanisms of sagging are still not well understood. In order to characterize sag resistance more precisely and to understand sagging mechanisms, both symmetrical and asymmetrical cyclic loading tests, rather than stress relaxation and the Bauschinger effect test, were carried out systematically on model material: industrial pure iron. It was chosen based upon the need to simplify the complicated microstructural effect on dislocation motion in suspension spring steels. Mechanical results were explored in detail, and slip band evolution and dislocation structures were also studied using an in situ optical microscope and transmission electron microscopy (TEM), respectively, to gain additional information on the cyclic plastic deformation process. In addition, the effect of the pre-strains on cyclic softening and cyclic creep was evaluated from the energy point of view. Based upon the present study, the following conclusions have been drawn: first, in contrast with tensile slip bands, fatigue slip bands showed much less multi-slip even at high cyclic peak stress levels and a large amount of cumulative cyclic plastic strain; second, mean stress was found to have a significant effect on the magnitude of cumulate cyclic creep strain; third, proof was obtained demonstrating that dislocation cell size decreases with increasing cyclic stress amplitude; forth, compressive cyclic creep was found in all pre-strained samples due to Bauschinger effect and such an effect was found to disappear completely in only 25-30 cycles and, therefore, this is a strong proof that sag deformation is mainly due to cyclic creep and cyclic deformation; finally, both increasing pre-strain level and decreasing cyclic peak stress resulted in less overall recoverable energy, and this stored energy is believed to promote the material to enter its stable stage of dislocation substructure more earlier, even though it may be released very slowly late in the deformation if the load is not symmetrical.

3:15 PM

Analytical Solutions at 180° Twist Boundaries in Cubic Crystals: *Peter Neumann*[1]; [1]Max-Planck Institute for Iron Research, Max-Planck-Str. 1, Duesseldorf D-40237 Germany

Grain boundaries are efficient stress raisers in elastically anisotropic materials. Because of the complexity of the underlying equations, the elastic incompatibility stresses are usually determined numerically. In a recent paper the transformation behavior of compliances and elastic constants in anisotropic cubic crystals was treated analytically and the equations of compatibility and stress equilibrium were solved analytically for the most simple case of a coherent twin boundary. This treatment is extended in the present paper to the whole class of 180° twist boundaries. The point is stressed that no additional shear stresses on the boundary are produced by the piecewise constant incompatibility stresses. The observed slip activity and crack initiation at the surface and on planes parallel to the twin boundary is due to an additional logarithmic stress singularity at the intersecting line between the twin boundary and the specimen surface. The strength and direction of these singular stresses is determined by the tractions of the

incompatibility stresses on the surface. They are given analytically as well.

3:40 PM Break

4:05 PM

Characterization of Dislocation Glide Kinetics during Cyclic Deformation by Strain Rate Change Tests: *George C. Kaschner*[1]; Jeffery C. Gibeling[2]; [1]Los Alamos National Laboratory, MST-8, Los Alamos, NM 87545 USA; [2]University of California, Dept. of Chem. Eng. and Matls., Davis, CA 95616 USA

A new experimental technique incorporating strain rate changes during cyclic deformation has been developed using plastic strain as the control variable. This technique was used to study the kinetics of dislocation interactions by evaluating the operational activation area and true stress as a function of cumulative plastic strain. In order to demonstrate the utility of this approach, it has been applied to three FCC metals: polycrystalline pure copper, 7075-T6 aluminum, and 304 stainless steel. These materials represent produce three distinct categories: pure FCC metals, precipitation-strengthened metals, and solution-strengthened metals. Plastic strain rate change tests were performed at plastic strain amplitudes between 0.2% and 0.6% from a base rate of $10^{-3}s^{-1}$ at room temperature. Initial values of the operational activation areas of copper evolved from approximately $5000b^2$ to $700b^2$ during cyclic loading to saturation. These values indicate a transition from forest dislocation cutting to cross-slip as the rate-controlling mechanism. Tests performed at saturation revealed a linear dependence of activation area on plastic strain amplitude. The back stress measured at saturation by extrapolating the activation area data compares favorably with the value determined from a Bauschinger analysis. The extrapolation method is an objective method of determining back stress and is especially suited for materials with asymmetrical hysteresis loops. The method is sensitive to the nuances of dislocation interactions of the various classes of materials tested; the characteristic responses of copper, 7075-T6 aluminum, and 304 stainless steel are distinct. Values of activation area correlate with the dominant rate controlling dislocation interaction mechanisms. In copper, these values correspond to a transition from cutting of forest dislocations to dislocation cross-slip. The results for 7075-T6 aluminum reveal that deformation is controlled by interactions with thermal obstacles in the form of GP zones and precipitates. Finally, this approach shows that rate-sensitive obstacles in the form of solutes control the cyclic deformation of type 304 stainless steel. This paper is based on work support by the National Science Foundation under Grant No. DMR-9208549.

4:30 PM

Cyclic Plasticity of Nickel at Low Plastic Strain Amplitude: *Y. Jia*[1]; D. J. Morrison[1]; J. C. Moosbrugger[1]; [1]Clarkson University, Dept. of Mech. and Aeronautical Eng., Potsdam, NY 13699-5725 USA

The cyclic plasticity of polycrystalline nickel was studied by accomplishing room temperature fully-reversed fatigue experiments at a constant plastic strain amplitude of 1.0x10-4 on nickel with a grain size of 290 μm. The cyclic plasticity behavior within a hysteresis loop was analyzed by measuring the curvature of the loop, $d^2\sigma_\Gamma/d\varepsilon_\Gamma^2$, where σ_Γ and ε_Γ are, respectively, the stress and total strain measured from the reversal point. In the classical Masing model of kinematic hardening, the curvature can be related to the frequency distribution of material volume element yield stresses. The results indicate that at low values of cumulative plastic strain, the cyclic plasticity within a loop approximates classical Masing kinematic hardening memory. However, at higher values of cumulative plastic strain, significant deviations from Masing memory are observed; and the behavior tends to reflect kinematic type III hardening as defined by Asaro[1]. The results will be discussed in terms of fundamental dislocation structures that are produced during low plastic strain amplitude cycling of pure fcc metals and the relationships between single crystal and polycrystal deformation behavior. This research was supported by the National Science Foundation under grant CMS 963407. [1]Asaro, R.J., 1975, Acta Metall., 23, 1255-1265.

4:55 PM

Micromechanisms of Fatigue Crack Growth in an a/b Titanium Alloy: *V. Sinha*[1]; S. Shademan[1]; A. B.O. Soboyejo[2]; W. O. Soboyejo[3]; [1]The Ohio State University, Dept. of Matls. Sci. and Eng., Columbus, OH 43210 USA; [2]The Ohio State University, Dept. of Food, Agri. Biolog. and Aero. Eng., Columbus, OH 43210 USA; [3]Princeton University, Dept. of Mech. and Aeros. Eng., Princeton Matls. Instit., Princeton, NJ 08544 USA

This paper presents the results of an experimental study of short and long fatigue crack growth in an a/b titanium alloy, Ti-6Al-4V. Differences between long fatigue crack growth rates at positive stress ratios are shown to be due largely to the effects of crack closure. Coarse Widmanstätten microstructures are also shown to exhibit higher intrinsic fatigue crack growth resistance than fine Widmanstätten or near-equiaxed a/b microstructures in the long crack regime. The improved fatigue crack growth resistance is associated with higher levels of roughness-induced crack closure and crack deflection. The fatigue fracture modes are summarized in fatigue mechanism maps before presenting multiparameter and mechanism-based fracture mechanics models for the prediction of fatigue crack growth.

Dislocations and Microscale Plasticity Modeling: Experimental Characterization of Dislocation Structures

Sponsored by: ASM International: Materials Science Critical Technology Sector, Materials Processing and Manufacturing Division, Structural Materials Division, Jt. Mechanical Behavior of Materials, Jt. Computational Materials Science & Engineering

Program Organizers: Elizabeth Holm, Sandia National Laboratories, Albuquerque, NM 87185-1411 USA; Diana Farkas, Virginia Polytechnic Institute and State University, Department of Materials Science and Engineering, Blacksburg, VA 24061 USA; Jeffrey Rickman, Lehigh University, Department of Materials Science and Engineering, Bethlehem, PA 18105-3195 USA; David J. Srolovitz, University of Michigan, Department of Materials Science and Engineering, Ann Arbor, MI 48109 USA; Vaclav Vitek, University of Pennsylvania, Department of Materials Science and Engineering, Philadelphia, PA 19104 USA

Monday PM — Room: Lincoln A
March 13, 2000 — Location: Opryland Convention Center

Session Chair: Diana Farkas, Virginia Polytechnic Institute, Matls. Sci. & Eng., Blacksburg, VA 24061-0237 USA

2:00 PM Invited

Observation and Modeling of Grain Boundary Dislocation Structure and Behavior: *Douglas L. Medlin*[1]; [1]Sandia National Laboratories, Thin Film and Interface Sci. Dept., Mail Stop 9161, 7011 E. Ave., Livermore, CA 94551 USA

Incorporating the localized effects of interfaces on materials properties is a significant challenge for large-scale materials simulations. Critical to improving such models is developing an improved understanding of the behavior of dislocations incorporated at grain boundaries. In this presentation, we discuss atomistic and continuum models for interfacial dislocations in relation to experimental observations made by transmission electron microscopy, focussing initially on interfacial dislocations in the FCC Σ=3 system. Though a simple geometry, the interfacial dislocations present in this system exhibit a rich and complex set of behavior. From an analysis of these defects, we provide insight into the larger scale coupling of dislocation motion, by both glide and climb processes, with grain boundary behavior. Finally, we discuss means of extending these results to boundaries of increasing crystallographic complexity. This work is supported by the U.S. DOE under contract DE-AC04-94AL85000, and in part by the OBES-DMS.

2:40 PM

Micro- and Macro-Scale Subdivision of a Bicrystal Based on Experiment and Plasticity: *A. Godfrey*[1]; V. Prantil[1]; D. E. Boyce[2]; D. A. Hughes[1]; H. R. Wenk[3]; P. Dawson[2]; [1]Sandia National Laboratory, MS 9403, P.O. Box 969, Livermore, CA 94551-0969 USA; [2]Cornell University, Sibley School of Mech. and Aerospace Eng., Ithica, NY 14853 USA; [3]University of California, Dept. of Geology, Berkeley, CA 94720 USA

Bicrystals of high purity aluminum have been deformed at room temperature to strains of 15-60%. The shape change and local crystal orientations were investigated by optical and scanning electron microscopy to characterize the macroscopic deformation pattern, thereby providing data at a length scale suitable for comparison with crystal plasticity model predictions. Preliminary calculations corroborate the shape changes away from the boundary, confirming that the crystal plasticity models resolve the average slip system activity reasonably well. However heterogeneous dislocation microstructures are observed in the transmission electron microscope (TEM). These microstructures have been extensively investigated in the TEM in order to determine the pattern of microscale slip activity, using both Burger's vector analysis and Frank formula analyses of the observed rotation boundaries. The implications of the observed microscale slip pattern for crystal plasticity models are then discussed. Part of this work was supported by the Office of Basic Energy Sciences, U.S. DOE, under contract No: DE-AC04-94AL85000.

3:00 PM

Studies of Microscale Plasticity in Bulk Samples Using ECCI: *Benjamin Andrew Simkin*[1]; Boon Chai Ng[1]; Martin A. Crimp[1]; Thomas R. Bieler[1]; [1]Michigan State University, Dept. of Matls. Sci. and Mech., 3536 Eng., East Lansing, MI 48824 USA

Electron channeling contrast imaging (ECCI) is a scanning electron microscopy technique that allows the direct imaging of dislocations and other deformation structures in the near-surface region of bulk crystals. ECCI forms contrast from regions of crystal distortion and rotation, such as occur near dislocation cores, twins, and grain boundaries. Although the contrast obtained using ECCI is similar to that found using diffraction contrast transmission electron microscopy, as ECCI uses bulk samples, it has the advantages that dislocations can be imaged under well defined stress states and large areas can be surveyed. Direct images of the dislocation structures associated with crack propagation and arrest has been assessed by imaging at crack tips and along crack paths in single crystal NiAl. Crack deflections and arrest are found to be directly associated with variations in dislocation generation in the crack tip zone. Deformation transfer across grain boundaries has been studied in relation to sample loading and macroscopic stress states in polycrystalline γ+α_{2} Ti-Al alloys. Strain transfer across grain boundaries is often found to occur by primary twinning inducing dislocation emission in adjacent grains from the twin/grain boundary intersection. Portions of this work were supported in part by the National Science Foundation (DMR\#9302040), Office of Naval Research (N00014-94-1-204), and the MSU Research Excellence Fund.

3:20 PM Break

3:40 PM

Temperature-Dependent Onset of Yielding in Dislocation-Free Silicon: Evidence of a Brittle-to-Ductile Transition: Robert H. Folk[1]; *David P. Pope*[1]; M. Khantha[1]; Vaclav Vitek[1]; [1]University of Pennsylvania, Dept. of Matls. Sci., LRSM, 3231 Walnut St., Philadelphia, PA 19104 USA

An investigation of the brittle-to-ductile transition (BDT) in silicon has been conducted. Photolithography has been used to produce silicon test specimens from semiconductor grade silicon wafers that were essentially defect free. No pre-cracks or additional dislocation sources were introduced into the samples. High temperature three-point bending tests of the samples reveals a well defined transition from brittle fracture of the specimens to complete yielding near 730°C at a crosshead displacement rate of 0.01 cm/min. Limited plasticity is observed prior to the transition but is insufficient to prevent crack propagation. In addition, between 735°C and 745°C there exists a temperature interval in which only limited plasticity is observed. This suggests that yielding of the samples is not limited by the mobility of dislocations. Instead the transition may be controlled by the nucleation of a sufficient density of dislocations within the material. This idea is further supported by experiments that were conducted at temperatures below 730°C in which samples were preloaded within the linearly elastic regime and then immediately retested. This preloading effectively enhanced the yield behavior of the samples with the degree of plasticity displayed by the samples a function of the magnitude of the preload. At the highest preloads complete yielding occurred, indicating that the BDT temperature had been lowered.

4:00 PM

Analysis of Anomalous Slip in Ta Single Crystals Using Optical Atomic Force, Orientation Imaging and Transmission Electron Microscopies: *Geoffrey H. Campbell*[1]; James S. Stölken[1]; Mehdi Balooch[1]; Wayne E. King[1]; Adam J. Schwartz[1]; [1]Livermore National Laboratory, Chem. and Matls. Sci. Directorate, P.O. Box 808, L-356, 7000 E. Ave., Livermore, CA 94551 USA

High purity Ta single crystals oriented for single slip were deformed in compression at 300K and 77K. The sample deformed at 300K exhibited wavy glide whereas the sample deformed at 77K exhibited anomalous slip. Sharp load drops were recorded in the stress-strain curve of the sample tested at 77K. Previous work attributes such unloading events to either the formation of large deformation twins or to the anomalous slip process itself. Orientation imaging microscopy was applied to probe lattice rotations occurring as a result of deformation in an effort to detect the presence of large deformation twins, none were found. Optical and atomic force microscopies were applied to map the slip traces appearing on the sample surface. Atomic force microscopy revealed that the fine structure within the rather coarse anomalous slip bands is comprised of atomistic scale slip lines organized into packets. These slip packets appear to account for the "fine slip traces" often observed within anomalous slip bands. Transmission electron microscopy was used to characterize the difference in dislocation structures between the specimens deformed at 300K and 77K. The fine scale dislocation structure within the anomalous slip bands is compared to the corresponding slip trace structure examined with atomic force microscopy. This work is performed under the auspices of U.S. Department of Energy and Lawrence Livermore National Laboratory under contract No. W-7405-Eng-48.

4:20 PM

Flow Stress Behavior of Polycrystalline OFHC Copper: *John E. Flinn*[1]; David P. Field[2]; Thomas M. Lilo[3]; Gary E. Korth[3]; Jenya Macheret[4]; [1]University of Idaho, 3450 S. 35 W., Idaho Falls, ID 83402 USA; [2]TSL Inc., 392 E. 12300 S., Ste. H, Draper, UT 84020 USA; [3]Idaho National Engineering and Environmental Laboratory, P.O. Box 1625, MSC2218, Idaho Falls, ID 83415-2218 USA; [4]U.S. Department of Energy, Idaho Operations Office, 850 Energy Dr., MS-1225, Idaho Falls, ID 83401 USA

The flow stress behavior of OFHC polycrystalline copper was evaluated from tensile specimens derived from cold roll and equal-channel angular extrusion processing. Prior to testing at room temperature, the specimens were annealed to provide grain sizes from 0.002 to 0.05 mm. The true stress-true strain behavior exhibit a parabolic pattern that correlates with four stages of hardening. In association with an increase in strain we observe: 1) dislocation source activation at the onset of plastic flow at annealing twin boundaries; 2) primary slip; 3) cross slip and forest hardening that is tied to stacking fault behavior; and 4) dynamic recovery. The tensile properties and analyses are accompanied by orientation imaging and transmission electron microscopy examinations and measurements.

4:40 PM

Effect of Temperature and Alloy Composition on Deformability of HfV_2+Ta C15 Laves Phase Alloy: *Won Yong Kim*[1]; David E. Luzzi[1]; David P. Pope[1]; [1]University of Pennsylvania, Matls. Sci. and Eng., 3231 Walnut St., Philadelphia, PA 19104 USA

The occurrence of twinning in Laves phase alloys is sensitive to alloy composition and deformation conditions such as strain rate and temperature. However, it remains unclear based on the existing work in the HfV_2+Nb system whether the twinning is solely stress-driven or whether there exists a critical temperature for twinning. Results in the HfV_2 system are somewhat ambiguous due to a fairly complex phase

equilibria and the predicted presence of a low temperature phase instability. We have recently found that alloying HfV_2 with Ta yields more extensive room temperature ductility by twinning in ternary Laves phase alloys that are more easily studied. In the present paper, Ta is again chosen as the ternary alloying element in HfV_2. HfV_2+Ta Laves phase based alloys with various compositions are produced by arc-melting and float-zone-melting. X-ray diffraction is used to analyze the crystal structures and lattice parameters for each sample investigated. Compression tests are conducted at temperatures down to near liquid helium temperatures using a specially designed testing apparatus. The effect of temperature and composition on mechanical properties is investigated to gain a better understanding of the mechanisms of twinning. Alloy microstructures are characterized using conventional and high-resolution TEM. Based on the obtained results, the deformation mechanisms will be discussed with particular attention given to the nucleation of twinning in the C15 cubic Laves phase.

5:00 PM

Strengthening Effects from Nitrogen Content and Grain Size on the Flow Stress Behavior of Type 316 SS: *Nikki Y. Pearce*[1]; John E. Flinn[2]; [1]Bechtel-Bettis Inc., Naval Reactors Facility, P.O. Box 2068, Idaho Falls, ID 83403-2068 USA; [2]University of Idaho, 3450 S. 35 W., Idaho Falls, ID 83402 USA

The influence of grain size and nitrogen content on the tensile behavior of Type 316 SS were evaluated. The focus of the analysis was on the flow stress behavior in terms of parabolic hardening with true strain. The results show a bilinear pattern, defined as parabolic stages II)p and III)p with increasing square-root of strain. The effects from grain size and nitrogen content (in solid solution) are primarily associated with the onset of plastic flow with very little influence on strain hardening. Stage II)p is associated with primary and secondary slip and Stage III)p with cross slip related dislocation forest hardening.

General Abstracts: Intermetallics I

Sponsored by: TMS

Program Organizers: Mark E. Schlesinger, University of Missouri, Department of Metallurgical Engineering, Rolla, MO 65409-0001 USA; Alton T. Tabereaux, Reynolds Metals Company, Smelter Technology Laboratory, Muscle Shoals, AL 35661-1258 USA; Dan J. Thoma, Los Alamos National Laboratory, Materials Science and Technology, Los Alamos, NM 87545-0001 USA; Patrice E.A. Turchi, Lawrence Livermore National Laboratory, Materials Science and Technology Division, Livermore, CA 94551 USA

Monday PM — Room: Bayou E
March 13, 2000 — Location: Opryland Convention Center

Session Chair: John J. Stephens, Sandia National Laboratories, Albuquerque, NM 87185-0367 USA

2:00 PM

On the Yield Strength Anomaly in CoTi and CoHf: *Ian Baker*[1]; M. Wittmann[1]; P. Bove[1]; [1]Dartmouth College, Thayer School of Eng., 8000 Cummings Hall, Hanover, NH 03755 USA

Mechanical tests have been performed on CoTi and CoHf alloys in order to determine whether the George-Baker vacancy-hardening model (Phil. Mag., 77 (1998) 737), which has been developed for FeAl, is applicable to the yield strength anomaly observed in these B2 compounds. Compression tests at elevated temperature reveal shifts in both the magnitude and temperature of the yield stress peak with changes in strain rate which are consistent with the model. However, quenching experiments, suggest that the vacancy concentrations at elevated temperature are much lower in CoTi and CoHf than in FeAl, and possibly too low for the vacancy hardening to be applicable. This work was funded by the National Science Foundation, Division of Materials Research through grant DMR-9812211 with Dartmouth College.

2:20 PM

Processing and Mechanical Properties of Mo-Si-B Alloys Containing High Volume Fractions of Mo_3Si and Mo_5SiB_2: *Joachim H. Schneibel*[1]; Hua-Tay Lin[1]; [1]Oak Ridge National Laboratory, Metals and Ceramics Div., P.O. Box 2008, Oak Ridge, TN 37831-6115 USA

Mo-Si-B alloys have melting points on the order of 2000°C. Their optimum composition involves a trade-off between processing, fracture toughness, and oxidation resistance. Mo-12Si-8.5B (at. %) can be fabricated by casting and contains approximately 30 vol.% Mo_3Si, 30 vol.% Mo_5SiB_2, and 40 vol.% α-Mo. The α-Mo occurs in the form of toughening inclusions. At room temperature this alloy exhibits a 3-point flexure strength of 500 MPa and a fracture toughness on the order of 10 MPa $m^{1/2}$. Its tensile creep properties, determined at 1200°C in argon, will be discussed. Mo-Si-B alloys with a continuous α-Mo matrix were fabricated by powder-metallurgical techniques and their mechanical properties and oxidation resistance will be compared to the corresponding properties for cast alloys. This research was sponsored by the Fossil Energy Advanced Research and Technology Development (AR&TD) Materials Program, U.S. Department of Energy, under contract DE-AC05-96OR22464 with Lockheed Martin Energy Research Corporation.

2:40 PM

Phase Formation and Interdiffusion in Silicides and Aluminides of Mo With and Without Re Additions: *Edward J. Ciecko*[1]; Mysore A. Dayananda[1]; [1]Purdue University, School of Matls. Eng., 1289 MSEE Bldg., West Lafayette, IN 47907 USA

Diffusion structures developed by interdiffusion between disks of Mo-aluminides in contact with disks of Mo, Si and Mo-silicides with and without additions of Re are investigated at selected temperatures between 700-1200°C. Phase formation and the effects of Al and Re on the interdiffusion of the components in the silicides of Mo will be discussed. Diffusion studies include an examination of the structures involving binary and ternary aluminides and silicides of the system Mo-Si-Re-Al. Diffusion structures will be described with the aid of diffusion paths. Interdiffusion coefficients for the silicides and aluminides observed in the diffusion structures will also be presented.

3:00 PM Break

3:20 PM +

Composition and Mechanical Properties of Mo_3Si: *Isai Rosales*[1]; Joachim H. Schneibel[1]; [1]Oak Ridge National Laboratory, Metals and Ceramics, P.O. Box 2008, Oak Ridge, TN 37831-6115 USA

The A15 phase Mo_3Si is an important constituent of a new class of silicides based on Mo-Si-B (D. M. Berczik, U.S. Patent No. 5,595,616, 1997; C. A. Nunes, R. Sakidja, and J. H. Perepezko, in "Structural Intermetallics 1997," TMS). In this research we will show that, contrary to published results, single-phase Mo_3Si is slightly off-stoichiometric. Its room temperature fracture toughness is on the order of 3.5 MPa $m^{1/2}$. When the deformation rate is high (10^{-3} s^{-1}), compressive deformation at 1400°C in argon often results in fracture associated with a decrease in load. At low deformation rates (10^{-5} s^{-1}) and 1400°C, fairly constant loads are reached after a few percent deformation. Partial substitution of Mo by Cr increases the high temperature strength. The high temperature strength of Mo_3Si will be compared to that of other silicides and A15 phases. This research was sponsored by the Division of Materials Sciences, U.S. Department of Energy under contract number DE-AC05-96OR22464 with Lockheed Martin Energy Research Corporation. I. Rosales acknowledges partial support from DGEP-FQ, Universidad Nacional Autonoma de Mexico.

3:40 PM

Influence of Aging Treatment on the Microstructure and Hardness of a Cr-Cr_2Ta Composite: *Peter K. Liaw*[1]; *Yuehui He*[1]; *C. R. Brooks*[1]; *C. T. Liu*[2]; [1]The University of Tennessee, Matls. Sci. and Eng. Dept., Knoxville, TN 37996-2200 USA; [2]Oak Ridge National Laboratory, Metals and Ceramics Div., Oak Ridge, TN 37831-6115 USA

A Cr-Cr_2Ta composite, as a new candidate of ultra-high temperature materials, is being studied. The excellent mechanical properties and good oxidation resistance of the composite at temperatures above

1000°C are provided by a solid-solution Cr(Ta) matrix reinforced with Cr_2Ta laves-phase plates. In this study, the effects of the as-cast process and aging treatment on the microstructure and hardness of a Cr-9.8 at.%Ta composite were examined. The hardness of the composite in the as-cast condition at room temperature decreased with increasing the aging temperature from 1000°C to 1300°C, which was due to the reduction of the solid-solution extent of the Cr(Ta) matrix. The morphology and formation mechanism of the microstructures of the composite in as-cast and aging-treatment states were explored. The orientation relationships between the Cr_2Ta phase and Cr(Ta) matrix were analyzed using transmission electron microscopy (TEM). This research is sponsored by the Fossil Energy Advanced Research and Technology Development (AR & TD) Materials Program under subcontract 11X-SP173V to the University of Tennessee with Dr. R. R. Judkins as the contract monitor.

4:00 PM

Effect of Temperature and Alloy Composition on Deformability of HfV_2+Ta C15 Laves Phase Alloy: *Won Yong Kim*[1]; David E. Luzzi[1]; David P. Pope[1]; [1]University of Pennsylvania, Matls. Sci. and Eng., 3231 Walnut St., Philadelphia, PA 19104 USA

The occurrence of twinning in Laves phase alloys is sensitive to alloy composition and deformation conditions such as strain rate and temperature. However, it remains unclear based on the existing work in the HfV_2+Nb system whether the twinning is solely stress-driven or whether there exists a critical temperature for twinning. Results in the HfV_2 system are somewhat ambiguous due to a fairly complex phase equilibria and the predicted presence of a low temperature phase instability. We have recently found that alloying $HfV_2$with Ta yields more extensive room temperature ductility by twinning in ternary Laves phase alloys that are more easily studied. In the present paper, Ta is again chosen as the ternary alloying element in HfV_2.

4:20 PM

Room Temperature Deformation of Cr-Based Laves Phase Alloys: *Won Yong Kim*[1]; David E. Luzzi[1]; [1]University of Pennsylvania, Matls. Sci. and Eng., 3231 Walnut St., Philadelphia, PA 19104 USA

Cr-based Laves phase alloys with AB_2 stoichiometry are promising material for high temperature structural applications due to their high melting temperatures, low density and potential resistance to corrosion and oxidation. Binary Laves phase alloys however, are extremely brittle at room temperature due to their complex crystal structure. Ternary alloying has been shown to yield room temperature deformability by twinning in HfV_2 with Nb or Ta. In the present study, refractory metals such as Hf, Ti, Ta and Nb are used as ternary alloying elements in various Cr-based Laves phases through consideration of chemistry, atomic size and electron-atom ratio. Laves phase alloys with a wide range of compositions are produced by arc-melting. Crystal structure, microstructure and lattice parameter analyses are carried out using optical microscopy and x-ray diffraction. We find that room temperature ductility is more common than currently understood with extensive room temperature ductility possible in $ZrCr_2$- and $NbCr_2$-based cubic Laves phase alloys after ternary alloying.

General Non-Ferrous Pyrometallurgy: Thermochemical Modeling and Physical Properties

Sponsored by: Extraction & Processing Division, Pyrometallurgy Committee

Program Organizers: Robert L. Stephens, Cominco Research, Trail, British Columbia V1R 4S4 Canada; Pekka Taskinen, Outokumpu Research Oy, Pori FIN-28101 Finland

Monday PM — Room: Bayou B
March 13, 2000 — Location: Opryland Convention Center

Session Chair: Pekka A. Taskinen, Outokumpu Research Oy, Pori FIN-28101 Finland

2:00 PM

Heat and Material Balance Model of the Kokkola Zinc Roaster Based on the HSC Chemistry 4.0 Software: *Antti Roine*[1]; Jens Nyberg[2]; [1]Outokumpu Research Oy, P.O. Box 60, Kuparitie 5, Pori 28101 Finland; [2]Outokumpu Zinc Oy, P.O. Box 26, Kokkola 67101 Finland

Sulfidic zinc concentrates are usually roasted in a fluidized bed furnace into sulfur-free oxide form. Metallic zinc is produced from this oxidic calcine using hydrometallurgical leaching, solution purification, and electrowinning stages. The roasting step is needed because zinc oxides are easier to dissolve than zinc sulfides using traditional leaching methods. The Kokkola Zinc Smelter uses various types of zinc concentrates and secondary materials as the feed mixture. Because the composition and particle size distribution of the feed mixture varies even on a daily basis, it is difficult to find the optimum process parameters for the process. Certain conditions may even cause difficult accretion problems or increase the amount of calcine in the process gas stream to an unacceptable level. A thermochemical heat and material balance model was developed in order to estimate the effects of different process parameters (temperature, process air coefficient, concentrate feed, oxygen enrichment, water feed, etc) on the heat balance, roasting temperature, and calcine composition. This model was constructed using the heat balance model of the HSC Chemistry 4.0 software. The prevailing chemical compounds in the concentrate and calcine were verified with the mineralogical analyses and equilibrium calculations. The roasting process seems to operate near the chemical equilibrium conditions, if the behaviour of the main components are considered. This paper describes briefly the basic principles of the calculation model and outlines the results with several diagrams and discussion. The calculated results were in reasonable agreement with the recent process air oxygen enrichment and water feed test campaigns carried out at Kokkola in 1999.

2:25 PM

Evaluation of New Process Parameters and Operating Conditions in Non-Ferrous Pyrometallurgy Through Thermochemical Modeling: *Florian Kongoli*[1]; Ian McBow[1]; [1]Flogen Technologies, P.O. Box 49529, CP Du-Musee, Montreal, Quebec H3T2A5 Canada

New operating conditions and process parameters are often necessary in today's industrial practice of non-ferrous smelting and converting in order to accommodate various new chemical compositions of mineral charges and environmental requirements or to conceive new and more efficient industrial technologies. An effective way to evaluate and predict these important parameters and conditions is thermochemical modeling, which decreases considerably the cost of pure experimental evaluation. This work presents thermochemical modeling of various phases in non-ferrous smelting and converting and their effective use in the evaluation of several factors such as the liquidus temperatures of slag, matte/slag/metal distributions, activities of crucial components etc. Several practical easy-to-use diagrams are

presented along with examples of cost decrease. Future developments are also discussed.

2:50 PM
The Correlation of Thermodynamic Properties of Multicomponent Liquid Alloy Systems: *Dajian Wang*[1]; *Tae-Kyu Kim*[1]; [1]University of British Columbia, Dept. of Metals and Matls. Eng., AMPEL 2355 E. Mall, Vancouver, BC V6T1Z4 Canada

To obtain the thermodynamic properties of a multicomponent liquid alloy system over the whole range of concentration at an arbitrary temperature, the free volume cell theory has been applied to derive the formula of activity coefficients of liquid solutions based on the infinite dilute solutions at some temperature. The linear relationship of logarithm of activity coefficients of binary dilute solutions versus reciprocal absolute temperature was verified in good agreement with the experimental values from the literature. The Monte-Carlo algorithm was used to calculate the nonlinear end value equations of binary systems, and then the free volume parameters obtained were directly correlated with the activity coefficients of liquid binary, ternary, quaternary, and quinary systems at an arbitrary temperature. The three dimensional diagrams of a-x-T of some binary systems representing the temperature and concentration dependence of activities were plotted. The calculated results regarding non-ferrous alloy systems have been statistically examined with the experimental values from the literature. Hence, this simple approach could be useful for analyzing thermodynamic properties of liquid alloy systems.

3:15 PM Break

3:30 PM
Viscosities of Some Binary and Ternary Slags in the System CaO-FeO-SiO2 with CaF2 Additions: *Fatemeh Shahbazian*[1]; Sichen Du[1]; Seshadri Seetharaman[1]; [1]Royal Institute of Technology, Metallu., Brinellv. 23, Stockholm 100 44 Sweden

Among the physical properties of slags, viscosity is very important in understanding the mass transfer phenomena in metallurgical processes. The viscosities of fayalitic slags are of great interest in the non-ferrous metal industry, with special reference to copper production. In an attempt to systematize the knowledge on slag viscosities, the present work was carried out. The viscosities of CaO-SiO_2, "FeO"-SiO_2 and CaO-"FeO"-SiO_2 slags with CaF_2 additions were carried out in the temperature range 1438-1762 K. The rotating cylinder method was used in the viscosity measurements. Crucibles and spindles made out of pure iron were employed. The slags were prefused before the measurements. In order to take into account the vaporization reactions involving CaF_2, pre- and post measurement samples of the slags were chemically analysed and the compositions were ascertained. The results show that in the case of the CaO-SiO_2 system, CaF_2 additions tend to decrease the viscosity, in accordance with the expectations. In the case of the "FeO"-SiO_2 system, at higher "FeO"/SiO_2 ratios in the slags, a reverse trend was observed. The measurements in the CaO-"FeO"-SiO_2-CaF_2 system indicate that the trends in this case are somewhat similar to the CaO-SiO_2 system. The results are discussed on the basis of a viscosity model for silicate melts developed in the present laboratory as well as the structural considerations of silicates.

3:55 PM
The Viscosity of Liquid Lead-Tin Alloys and its Temperature Dependence: *José Deodoro Trani Capocchi*[1]; [1]University of São Paulo, Dept. of Metallu. and Matls. Eng., Polytechnic School, Av. Prof. Mello Moraes, 2463, São Paulo, SP 05508-900 Brazil

Viscosity of liquid Pb-Sn alloys has been measured by the rotational viscometer method in the temperature range from 50 K above their respective liquidus temperature to 823 K. The results are accurate to within ±1.0%. The variation of viscosity with temperature followed the Arrhenius-type equation $m=m_0.exp^{(Q/RT)}$. The composition dependence of the isothermal viscosity and the activation energy for viscous flow has not shown anomalous changes at the eutectic composition of the Pb-Sn system.

4:20 PM
Removal of Copper from Slags with the Aid of Reducing and Sulfiding Gas Mixtures: *Andrey V. Tarasov*[1]; S. D. Klushin[1]; [1]Gintsvetmet Institute, State Rsch. Instit. of Non-Ferrous Metals, 13 Acad. Korolyov St., Moscow 129515 Russia

The most common method for decreasing the copper content of slags from autogenous smelting of copper sulfide concentrates is treatment of molten slag in an electric furnace, among other things, by adding solid reducing and sulfiding agent, i.e., pyrite. One of the drawbacks of this technique is production of final slag with a copper content of about 0,5%. An innovative method was tested based on treatment of molten slag from autogenous smelting process by a gaseous mixture of sulfur dioxide and methane at a ratio of CH_4:SO_2=1:(3,0-4,7) in the presence of oxygen. Cleaning of slag to remove copper was carried out at a pilot plant in the second zone of the furnace where slag was maintained within a range of 1250-1350°C. Reactions in the SO_2-O_2-CH_4 system proceed at a high rate at temperatures within 1100-1300°C to form reducing-sulfiding agents: H_2S, S, COS, CO, CO_2, H_2, H_2O. The required amount of the gas mixture is in the order of 100-150 Nm^3 per 1 tonne of slag. A decrease in the ferric iron concentration (Fe^{3+}) from 10-15% to 2-3% results in lower copper solubility in slag, while agitation of the melt with gas leads to an accelerated separation of the sulfide phase formed and the slag. The copper content of the final slag is about 0,12-0,14%. The yield of bottom matte is 7-10% of the weight of the slag processed and its copper content is about 12-15%. The matte with a copper content of 50-55% sent to converting is a mixture of bottom phases from two zones of the smelting furnace, i.e., from the settling zone and from the slag decopperizing zone. Off-gases from both zones are mixed inside the furnace and sent to a sulfuric acid plant. This process has been proposed for commercial introduction at two smelters in Russia and the CIS Republics.

High-Temperature Superconductors: Synthesis & Processing

Sponsored by: Electronic, Magnetic & Photonic Materials Division, Structural Materials Division, Superconducting Materials Committee

Program Organizers: U. Balu Balachandran, Argonne National Laboratory, Argonne, IL 60439 USA; Pradeep Haldar, Intermagnetics General Corporation, Latham, NY 12110-0461 USA; Chandra Pande, Naval Research Laboratory, Materials Science and Technology Division, Washington, DC 20375-5000 USA

Monday PM — Room: Canal D
March 13, 2000 — Location: Opryland Convention Center

Session Chair: Donglu Shi, University of Cincinnati, 498 Rhodes Hall, Cincinnati, OH 45221 USA

2:00 PM Invited
Dopants in Processing of High Temperature Superconductors: *Sharmila Mitra Mukhopadhyay*[1]; [1]Wright State University, Mech. & Matls. Eng., Colonel Glenn Hwy., Dayton, OH 45432 USA

The possibilities of "Dopant enhanced texturing (DET)" of perovskite superconductors will be discussed. It is seen that an anionic dopant such as Br on the surface of superconducting Y-Ba-Cu-O (YBCO) results in enhancement of sintering and grain growth rates without any adverse compositional or crystallographic changes. This effect will be compared with that of a cationic dopant (Yb) that lowers the eutectic temperature of the 123 structure. Our studies indicate that these dopants may cause activated sintering and/or enhanced liquid phase sintering. Possible atomistic mechanisms underlying all these effects will be discussed. Since large domain sizes and preferred orientations are key to electrical and levitation properties of these materials, the possibility of adding a dopant that increases grain growth rate without increasing processing temperature may be very useful in controlling texture. Future studies that can make this a technological reality will be discussed.

2:30 PM Invited

Dislocations and Plastic Flow in Flux-Line Lattices of High-Temperature Superconductors: *David O. Welch*[1]; [1]Brookhaven National Laboratory, Dept. of Appl. Sci., Bldg. 480, P.O. Box 5000, Upton, NY 11973-5000 USA

Since the classic work of E. J. Kramer[1] and many others during the 1970's, it is known that for conventional superconductors, under conditions which depend on the magnetic flux density and the density, topology, and spatial distribution of pinning centers, the onset of flux flow, and thus the critical current density (J_c), results from the plastic deformation of the flux line lattice. Recently by means of advanced methods of electron microscopy, Tonomura et al.[2] have imaged a variety of types of plastic flow in FLLs within $Bi_2Sr_2CaCu_2O_{8+\delta}$ crystals. Previously, within the context of a simple analytical theory based on the theory of dislocations and plastic flow in metals and alloys, I have shown how stress states arise in FLLs and discussed the role of temperature, current density, and pinning center strength, topology, and distribution in determining whether plastic shear of the FLL or depinning limits the critical current density.[3] In this paper, I will discuss how the character of dislocations in the FLL and its consequent shear strength depend on the anisotropic, layered nature of cuprate superconductors and will describe a theory of flux creep, flux flow, and the EJ characteristics of HTS materials based on dislocations and the plasticity of FLLs in cuprates. [1.]E. J. Kramer, J. Appl. Phys. 49, 1360 (1973). [2.]A. Tonomura et al., Nature 397, 308 (1999). [3.]D. O. Welch, IEEE Trans. Appl. Supercond. 3, 1476 (1993). This research was supported by the US. Department of energy, Division of Materials Sciences, Office of Basic Energy Sciences under Contract No. DE-AC02-98CH10886.

3:00 PM Invited

Congruent Growth Mechanism of Peritectic Phase in Undercooled Nd-Based Superconducting Oxides: *Kosuke Nagashio*[1]; Yuzuru Takamura[2]; Kazuhiko Kuribayashi[2]; Yuh Shiohara[3]; [1]The University of Tokyo, Matls. Sci. Dept., 7-3-1 Hongo, Bunkyo-Ku, Tokyo 113-8656 Japan; [2]The Institute of Space and Astronautical Science, 3-1-1 Yoshinodai, Sagamihara, Kanagawa 229-8510 Japan; [3]Superconductivity Research Laboratory, ISTEC, 1-10-13 Shinonome, Koto-ku, Tokyo 135 Japan

Congruent growth mechanism of a peritectic phase, $NdBa2_{Cu2}O7_{-x}$ (Nd123), from undercooled melt below a peritectic temperature (T_p) is discussed from the viewpoint of a phase selection theory based on a competitive growth in the peritectic system for free growth condition. The seeding experiment to clarify the temperature dependence of phase appearance shows that the volume fraction of Nd123 drastically increased when the seeding was carried out at the temperature below T_p. The growth velocity of the Nd123 phase measured concurrently well agreed with the theoretical calculation based on the phase selection theory where it was assumed that melting point of the Nd123 phase is T_p and the Nd123 phase grow congruently from undercooled melt below T_p. These results suggest that the driving force of the Nd123 phase is activated below T_p, not the hypothetical congruent melting point.

3:30 PM Invited

Reactive Field Assisted Sintering of BSCCO-Ag_2O Ceramic Produced from Freeze Dried Precursor Powders: *Petre Badica*[1]; George Aldica[1]; Joanna R. Groza[2]; M. C. Bunescu[3]; S. Mandache[1]; [1]National Institute for Materials Physics, POB MG-7, Bucharest, Magurele R-76900 Romania; [2]University of California-Davis, Chem. Eng. and Mat. Sci. Depts., One Shields Ave., Davis, CA 95616 USA; [3]Metav-S.A., Pob 18/3, Bucharest, Romania

Nitrate freeze dried powder (Bi:Pb:Sr:Ca:Cu=1.7:0.3:2.0:2.5:3.5) was decomposed at 750°C for 60 min. in air and mixed with commercial Ag_2O (1.2% wt.). Two types of samples with and without silver oxide addition were processed by Reactive-Field-Assisted-Sintering Technique (RFAST) at 750°C for 4 minutes under a pressure of 17.5 MPa in vacuum. Final heat treatments were applied at 800-870°C for 70-200 h. RFAST-pellets produced from precursor powder with and without Ag_2O have shown different behavior. Reaction of 2212-phase formation during RFAST was sluggish in Ag_2O-BSCCO pellets. No 2223-phase could be observed after RFAST processing, but this phase formed during final heat treatment. The role of Ag_2O during BSCCO-RFAST is discussed.

Hume Rothery Award Symposium; Phase Transformations and Evolution in Materials: Session I

Sponsored by: Structural Materials Division, Electronic, Magnetic & Photonic Materials Division, Alloy Phases Committee

Program Organizers: Patrice E.A. Turchi, Lawrence Livermore National Laboratory, Materials Science and Technology Division, Livermore, CA 94551 USA; Antonios Gonis, Lawrence Livermore National Laboratory, Livermore, CA 94551-0808 USA

Monday PM — Room: Johnson A/B
March 13, 2000 — Location: Opryland Convention Center

Session Chairs: Robert W. Cahn, FRS, Cambridge University, Matls. Sci. and Metallu., Cambridge CB2 3QZ England; Peter W. Voorhees, Northwestern University, Matls. Sci. and Eng. Dept., Evanston, IL USA

2:00 PM Opening Remarks

2:05 PM Keynote

Theoretical Characterization of Alloy Structures at Microscopic and Mesoscopic Scales: *Armen G. Khachaturyan*[1]; [1]Rutgers University, Cer. and Matls. Eng. Dept., Piscataway, NJ 08855-0909 USA

Development of the theory of alloy structure from atomic to nanoscale level is discussed. It is shown that the structure on the atomic scale is described by the occupation probability function, which can be formulated in terms of Static Concentration Waves. Amplitudes of the waves are the long-range order parameters, the wave vectors are the superlattice reciprocal lattice vectors. This approach is especially effective in the mean-field approximation. However, it was also successfully used if the correlation effects are taken into account. The Concentration Wave method describes both the atomic scale and the nanoscale (if the variation of lro parameters becomes considerable). With this feature, this method provides a bridge between the scales. It is shown how this method can be used to make an accurate transition to the Phase Field theory of evolution of the microstructure on the mesoscopic scale. The Phase Field theory of the mesoscopic microstructure evolution in coherent structurally inhomogeneous alloys with multivariant domains of ordered intermetallics is discussed. The evolution is driven by the minimization of transformation strain. This theory is based on the Phase Field micromechanics incorporated in the alloy thermodynamics. This approach allows one to realistically simulate the mesoscopic microstructure evolution for a wide spectrum of materials (metal and ceramics) with different types of transformations (diffusional and displacive). Input data required to carry out the computer simulation are the crystal lattice parameters, compositions and elastic moduli of phases, and the interfacial energy.

3:00 PM Invited

Application of Khachaturyan's Elasticity Theory to Modeling Coherent Phase Transformations and Structural Defects: *Long-Qing Chen*[1]; [1]Penn State University, Matl. Sci. and Eng. Dept., 118 Steidle Bldg., University Park, PA 16802 USA

One of many Khachaturyan's major contributions to materials science is his elasticity theory for any arbitrary coherent microstructures. It has become a routine tool for many experimentalists to predict the equilibrium shapes and habit planes of precipitates using independent parameters such as lattice parameters and surface energy, and to interpret their experimental observations. In the last few years, it

has also become an integral part of phase-field modeling of coherent phase transformations in solids. In this talk, a brief review will be given for the application of Khachaturyan's elasticity theory to phase-field simulation of microstructure evolution during coherent phase transformations. In particular, the effect of an applied external load (strain/stress) or internal stress fields created by local defects such as dislocations and point defects will be discussed. A simple method for introducing the local fields created by structural defects into the phase-field model of coherent phase transformations will be presented. This method will be applied to the diffusional nucleation and growth of coherent precipitates at dislocations and the effect of local tetragonal distortions on a cubic to tetragonal transformation. It will be shown that structural defects can have a significant influence on coherent phase transformations. For example, nucleation at a dislocation may become barrierless as a result of coupling between the coherency strain and the local fields by the dislocations.

3:30 PM Break

3:45 PM Invited

Gamma' Precipitate Shape Evolution and Splitting in Ni-Based Alloys: *Alan J. Ardell*[1]; Dongman Kim[1]; [1]University of California-Los Angeles, Matls. Sci. and Eng., 6531-G BH, Los Angeles, CA 90024-1595 USA

It is well known that the shapes of gamma'-type (Ni3X, X = Al, Si, Ti and combinations thereof) precipitates in aged Ni-X alloys change from spheres to cuboids as their size increases. When the volume fraction is small, generally less than 0.03 to 0.04, the shapes continue to evolve as the particles grow by diffusion-controlled coarsening. They become nearly perfect cubes, which evolve into a concave cuboidal shape at yet larger sizes. In alloys cooled directly from the solution-treatment temperature to the aging temperature the concave cuboidal particles undergo splitting transitions into either pairs of parallel plates or groups of 8 cuboids. These types of transitions are consistent with predictions of computer simulation experiments of Khachaturyan and his co-workers. In alloys that are quenched and aged, which is the typical heat-treatment procedure in our laboratory, the evolution of shapes into concave cuboids is observed, but splitting of these particles (Ni3Al and Ni3Ti, for example) has not been seen. Experiments are in progress to determine whether there is something inherent in the heat-treatment procedure that stimulates the splitting transition. We will also present the results of aging experiments on Ni-Ga and Ni-Ge alloys containing small volume fractions of Ni3Ga and Ni3Ge, in which the shape transitions have not been previously characterized. This research is supported by the National Science Foundation.

4:15 PM Invited

Coherency Strain in Elastically Inhomogeneous Systems: *Jong K. Lee*[1]; [1]Michigan Technological University, Dept. of Metallu. and Matls. Eng., 1400 Townsend Dr., Houghton, MI 49931 USA

Professor Khachaturyan advanced a multitude of seminal works on strain effects in crystalline solids, especially in elastically homogeneous systems. His theories shed light, among others, on the role of both elastic anisotropy and tetragonal misfit strain, which led us to clear understanding of particle splitting in nickel-based superalloys and strain-induced ordering behavior in interstitial alloys. This presentation is to complement his works with recent findings on coherency strain effects in elastically inhomogeneous systems, i.e., in solids where the competing phases have different elastic constants. The origin for particle splitting has been usually understood in terms of anisotropic strain energy. This view is incomplete in light of recent theoretical works demonstrating that a particle in an isotropic system splits into multiple particlets. Splitting phenomena can be classified into a commensurate and an incommensurate elastic instability. In the former, a non-equilibrium elastic state may cause particle splitting provided that relaxation of the excess strain energy can overwhelm the accompanying interfacial energy increase. The second case of incommensurate instability arises when the anisotropy ratios of the precipitate and matrix phase have opposite signs, for example, when the elastically soft direction of the matrix is parallel to the hard direction of the particle phase. One of the driving forces for ordering is long known to be the relaxation of strain energy due to difference in atomic size. Coherency-induced ordering in a substitutional alloy is examined in a simple model with a two-dimensional square lattice. When both elastic and chemical interactions join together for ordering, the order-disorder transition temperature is raised to a value greater than the sum of the two individual cases. Other aspects of elastic inhomogeneity effects, including a case with tetragonal misfit strains, will be discussed.

4:45 PM Invited

Generalized Phase Field Modeling of Microstructural Evolution in Solids: Incorporation of Rigid-Body Motion of Grains and Mobility/Energy Anisotropy of Grain Boundaries: *Yunzhi Wang*[1]; Andrei Kazaryan[2]; Chen Shen[1]; Bruce R. Patton[2]; [1]The Ohio State University, Matls. Sci. and Eng., 2041 College Rd., Columbus, OH 43210 USA; [2]The Ohio State University, Phys. Dept., 174 W. 18th Ave., Columbus, OH 43210 USA

The phase field approach to microstructural evolution during solid state phase transformations, originally popularized by Armen Khachaturyan and his coworkers, has received an increasing amount of attention in the last few years. Several reasons may have contributed to its popularity. For example, it is able to simulate realistic microstructures and their evolution during both diffusional and diffusionless transformations under conditions of high volume fraction, elastic interactions arising from both internal lattice misfit and external fields, and multiple ordered domains and orientation variants. However, modeling microstructural evolution in solids containing grain boundaries and free surfaces demands that the model accounts for the movement of individual particle as a rigid body. Further more, the mobility and energy of grain boundaries are usually anisotropic rather than isotropic in may solids. In the current formulation of the phase field model for solid state microstructural evolutions, both rigid-body motion and crystal anisotropy are not considered. In this presentation, recent efforts in extending the phase field method for simulating phenomena such as sintering and anisotropic grain growth will be discussed in the context of incorporating rigid-body motion of grains and mobility/energy anisotropy of grain boundaries. These advances allow different phenomena occurring during sintering and similar processes to be simulated in a single, consistent methodology. A number of problems which require consideration of rigid-body motion and anisotropic grain boundary properties will be addressed.

International Symposium on Global Innovations in Materials Processing and Manufacturing: Tutorials and Overviews of Solid Free Form Fabrication Techniques

Sponsored by: Materials Processing and Manufacturing Division

Program Organizers: David L. Bourell, University of Texas, Mechanical Engineering Department, Austin, TX 78712-1063 USA; Iver Anderson, Iowa State University, Ames Laboratory, Ames, IA 50011-3020 USA; James W. Sears, Lockheed Martin, KAPL Inc., D2, 114, Schenectedy, NY 12301 USA; John E. Smugeresky, Sandia National Laboratories, Department 8724, Livermore, CA 94551-0969 USA; Dan J. Thoma, Los Alamos National Laboratory, Materials Science and Technology, Los Alamos, NM 87545-0001 USA; Srinath Viswanathan, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6083 USA; Rob Wagoner, The Ohio State University, Department of Materials Science and Engineering, Columbus, OH 43210 USA

Monday PM — Room: Canal E
March 13, 2000 — Location: Opryland Convention Center

Session Chair: John E. Smugeresky, Sandia National Laboratory, Dept. 8724, Livermore, CA 94551 USA

2:00 PM
Overview of Direct Fabrication Processes and Materials-An Industrial User Perspective: *W. R. Schmidt*[1]; D. L. Anton[1]; A. F. Giamei[1]; [1]United Technologies Research Center, East Hartford, CT 06108 USA

Computer-based design and visualization technologies are critical for achieving significant reductions in time-to-market for new products and production parts. In parallel with this revolution has been the development of additive manufacturing technologies, which can rapidly and directly render these complex computer-based ideas into physical articles via a Solid Freeform Fabrication (SFF) process. SFF opportunities exist when conventional manufacturing techniques cannot easily be used, due either to high processing costs, one-of-a-kind or low volume production levels, geometry limitations, long lead times, and/or specialty materials. This presentation will provide an overview of several commercial and developmental techniques for directly fabricating parts and tools for aerospace or commercial use, including a description of planned usage in the manufacturing environment. Examples of current capabilities, limitations, and challenges, along with a wish list of process and product attributes will be discussed.

2:30 PM
Tutorial on Stereolithography: *Paul F. Jacobs*[1]; [1]Express Tool, Warwick, RI USA

This presentation will explain the fundamental principles underlying the stereolithography process. Information will be provided regarding the nature of the UV laser radiation/photopolymer reaction, the log linear "working curve" relationship between cure depth and laser exposure, the basic parabolic cylinder cured volume element, and the functional dependence of the cured line-width. The evolution of build styles, from "Tri-Hatch" to "WEAVE" to "STAR-WEAVE" to ACES and QuickCast will also be covered. Specific applications involving the generation of QuickCast Patterns for the investment casting of functional metal components, the use of ACES models for photo-stress analysis, and the Direct AIM process for prototype plastic injection molding will also be described.

3:00 PM
Laminated Object Manufacturing (LOM): *Mukesh K. Agarwala*[1]; [1]University of Dayton, Rsch. Instit., 300 College Park, Dayton, OH 45469-0172 USA

Laminated Object Manufacturing (LOM) is a Rapid Prototyping process that uses feed materials in the form of sheets. The LOM process fabricates a part by laminating sheets of material and cutting out cross-sections on each sheet layer. Commercially the LOM process offers adhesive backed paper as the material of choice to its users. The fabricated LOM parts from paper appear like wood models and are used in a variety of applications. This tutorial will discuss the basics of the LOM process and review the state-of-the-art in LOM technology. Due to sheet based processing, the LOM process has also been developed to use green ceramic and metal sheet materials to fabricate ceramic and metal parts. Developments in the LOM processing of ceramic, metal, and fiber reinforced composites will also be reviewed.

3:30 PM Break

3:40 PM
Fused Deposition Modeling (FDM): *Mukesh K. Agarwala*[1]; [1]University of Dayton, Rsch. Instit., 300 College Park, Dayton, OH 45469-0172 USA

Fused Deposition Modeling (FDM) is a Rapid Prototyping process that extrudes and deposits a thermoplastic material in selective areas as defined by the CAD data. The extruded material solidifies as it is deposited onto a substrate or onto previously built layers. Commercially the process offers a variety of thermoplastic materials for fabrication of prototypes. The FDM thermoplastic parts can be used in a variety of applications, including certain functional applications. This tutorial will describe the FDM process and review the state-of-the-art in the FDM technology. Several developments are currently underway to apply the FDM technology to the processing of ceramics and metals. Ceramic and metal processing by FDM process employs a powder injection molding type of green feedstock to fabricate green ceramic and metal components. This presentation will review the developments taking place in the FDM processing of metals and ceramics.

4:10 PM
Tutorial on Selective Laser Sintering: *Christian Nelson*[1]; David Bourell[2]; [1]DTM Corporation, 1611 Headway Circle, Bldg. 2, Austin, TX 78754 USA; [2]University of Texas, Mech. Eng., MC C2200, Austin, TX 78712-1063 USA

The SLS® Selective Laser Sintering process is a rapid prototyping (RP) process which uses a laser to selectively fuse powdered materials together, creating objects layer by layer. The SLS process has the unique advantage of processing a broad range of materials in a single RP platform. Plastic, ceramic, and metal material systems are commercially available, and the development of new materials is ongoing at a number of universities in around the world. This discussion will touch on the technical issues of processing the different types of material systems, but will focus on the processing of two types of metal material systems.

4:40 PM
Tutorial on Selective Area Laser Deposition (SALD) of Ceramics: *Harris Marcus*[1]; [1]University of Connecticut, Instit. of Matls. Sci., Storrs, CT 06269-3136 USA

The processing necessary to do solid freeform fabricating (SFF) from vapor phase precursors will be described. Included will be a description of the processing instrumentation used. The nature of the gas/laser beam interactions and specific systems studied will be described. This will include both selective area laser deposition (SALD) and SALD vapor infiltration (SALDVI) SFF approaches. SALD is direct writing from the localized decomposition from the gas phase and SALDVI involves infiltration into powder layers to create the SFF shapes. The range of processing parameters and their influence on the character of the deposits will be described.

5:10 PM
Overview of Rapid Solidification Phenomena in Direct Metal Deposited Materials: *Dan J. Thoma*[1]; *John E. Smugeresky*[2]; [1]Los Alamos National Laboratory, Los Alamos, NM 87545 USA; [2]Sandia National Laboratory, Livermore, CA 94551 USA

Direct metal deposition processes display microstructures that are consistent with rapid solidification phenomena. For example, a continuous liquid/solid interface is maintained while achieving constant cooling rates that can be varied between 10 to 10^5 K s^{-1} and solidification growth rates (that scale with the beam velocity) ranging up to 10^{-2} m s^{-1}. Moreover, microsegregation profiles do not necessarily adhere to interfacial equilibrium conditions at the solid/liquid interface. The rapid solidification results from approximately 100 micron layers being epitaxially deposited onto a cooled, prior substrate. Traditional rapid solidification techniques rely on at least one thin dimension from which heat can be rapidly removed. Direct metal deposition techniques also rely on a thin deposition layer, but permits bulk rapidly solidified samples to be produced. The characterization of the rapid solidification behavior and the implications related to the properties of fabricated materials will be discussed.

International Symposium on Iridium: Structures and Properties

Sponsored by: Structural Materials Division, Refractory Metals Committee

Program Organizers: Evan K. Ohriner, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6083 USA; H. Harada, National Research Institute for Metals, Tsukuba, Ibaraki 305 Japan; R. D. Lanam, Engelhard-CLAL, Careret, NJ 07008 USA; Peter Panfilov, Ural State University, Ekatrinburg 62001 Russia

Monday PM — Room: Jackson A/B
March 13, 2000 — Location: Opryland Convention Center

Session Chairs: Hiroshi Harada, National Research Institute for Metals, Ibaraki 305-0047 Japan; Joseph G. Biondo, Engelhard-CLAL LP, Cateret, NJ 07008 USA

2:00 PM Invited

On Specific Features in Mechanical Behaviour of Iridium: *P. Panfilov*[1]; [1]Urals State University, Lab. of Strength, Ekaterinburg 62001 Russia

There is only one face centred cubic metal whose mechanical behaviour may be called “puzzling.” Many tests have shown that high purity iridium could be both a highly plastic and a brittle substance simultaneously. This anomaly is the subject of this paper. Octahedral slip is the main deformation mechanism in iridium, while the contributions of mechanical twinning and other mechanisms are insufficient for deformation over wide temperature ranges. Brittle transcrystalline fracture or cleavage is the inherent tensile fracture mode observed in the necked region of polycrystalline samples or after considerable elongation of single crystals. Analysis of the evolution of transcrystalline cracks has shown that the inclination to cleavage is a property of bulk crystals. Recrystallization leads to catastrophic decrease in the plasticity of iridium: grain boundaries are dangerous places in polycrystalline metal. However, the intercrystalline brittleness of iridium does not depend on contaminants only.

2:30 PM

Types and Fundamental Properties of States Occupied by 57 Co Atomic Probes in the Grain-Boundary Core and Adjacent Regions of the Lattice in Polycrystalline Iridium: V. N. Kaigorodov[1]; *S. M. Klotsman*[1]; A. V. Ermakov[2]; V. K. Rudenko[2]; A. N. Timofeev[1]; N. I. Timofeev[2]; [1]Institute of Metal Physics, Urals Div. of Russian Acad. of Sci., S. Kovalevskaya 18, Ekaterinburg 620219 Russia; [2]Non-Ferrous Metals Processing Plant, The Head of Rsch. Ctr., Lenin Ave. 8, Ekaterinburg 610014 Russia

Iridium polycrystals with the grain size of the order of $2\text{-}10^{-4}$ m were produced by deformation of a pure (4N) single crystal of iridium at 800°C and its recrystallization in a ultra-high vacuum furnace at 1273 K for 2 hours. Radioactive ^{57}Co tracers diffused into an iridium polycrystal at 500K under conditions of preferable intercrystallite diffusion (at temperatures below 800K). The examination by the method of nuclear gamma resonance spectroscopy showed that only two types of states in the intercrystallite diffusion (ICD) zone, one in the core of the intercrystallite conjugation regions and the other in adjacent regions of the lattice, were populated even at extremely low temperatures of the diffusion introduction of the ^{57}Co atomic probe in poly-Ir. These states differed by isomer shifts, local Debye temperatures, and Curie temperatures of magnetic ordering of residual magnetic active impurities.

2:50 PM

An Atomistic Study of the Dislocation Core Structure and Interatomic Interaction Potentials in Iridium and Rhodium: *Ludmila Yakovenkova*[1]; Bella Greenberg[1]; Yurii Shamanaev[1]; Lidia Karkina[1]; [1]Institute of Metal Physics, Ural Div. of Russian Acad. of Sci., Ekaterinburg 620219 Russia

The interatomic potential for Ir, which describes with high accuracy phonon spectra, lattice properties, including energy characteristics of point defects was obtained. The analogous potential is plotted for Rh. The structure and energy stacking faults as well as dislocation core was calculated by computer simulation method. Simulation of screw and edge dislocations showed that these split effectively on the {111} planes. Comparative analysis of the structure and energy of {110} planar defects in Ir, Rh and Cu was carried out. It is shown that, contrary to the case of copper, the stacking-fault-energy surfaces of iridium and rhodium exhibit minima for the shear by the vector a/4<110>. Analysis of the gain in energy upon dissociation of the a/2<110> dislocations shows that in iridium and rhodium this dislocation dissociates into two a/4<110> partials on the {110} planes.

3:10 PM

Investigations of Microstructure-Property-Relationships in Iridium: *J. Merker*[1]; D. F. Lupton[1]; H. -J. Ullrich[2]; M. Schlaubitz[3]; B. Fischer[4]; [1]W. C. Heraeus GmbH & Company KG, Matls. Tech. Div., Dev. Dept., Heraeusstrasse 12-14, Hanau D-63450 Germany; [2]Technical University Dresden; [3]Infineon Technologies Dresden GmbH & Company OHG; [4]University of Applied Science, Jena

Because of its chemical stability and the high melting point of 2454°C iridium is especially suitable for applications at the highest temperatures. In spite of its face-centered cubic lattice structure iridium, even of very high purity, tends to brittle behaviour both in hot and cold forming. It shows unusually strong work hardening in forming. Therefore, the formability of iridium presents a technical problem in the manufacturing of semi- and finished products. The formability and the strength properties are essentially influenced by the generation of lattice distortions during forming. In the same way, the influence of trace impurities on mechanical properties is known. Investigations by means of the back reflection X-ray divergent beam technique and the Kossel technique stimulated by an electron beam were accomplished at the TU Dresden as a contribution to explaining the causes of brittleness. The Kossel technique stimulated by an electron beam shows a high sensitivity with regard to mechanically influenced surfaces. It was possible to eliminate the influence of the surface work-hardened layer on the generation of Kossel interferences by using high energy and high intensity synchrotron radiation. The influence of selected manufacturing conditions (rolling and annealing conditions) on the real structure of compact samples was shown by using the back reflection X-ray divergent beam technique. High dislocation densities, local mechanical distortions in the lattice and small angle grain boundaries were indicated. These are the main reasons for the difficult processing of iridium. By means of microhardness measurement under testing force, both the elastic and plastic components of the impression and deformation processes were determined. Significant differences in the hardness were indicated dependent on the different manufacturing conditions. These results correspond with the investigated dislocation densities.

3:30 PM Break

3:40 PM

The Distribution of Ir in Ni-Based Single-Crystal Superalloys: *H. Murakami*[1]; T. Yokokawa[1]; Y. Koizumi[1]; *H. Harada*[1]; [1]National

Research Institute for Metals, High Temp. Matls. 21 Project, 1-2-1 Sengen, Tsukuba Science, Ibaraki 305-0047 Japan

The addition of platinum group metals (PGMs) to Ni-based superalloys are being considered for the next generation superalloys with higher temperature capabilities. Among PGMs, Ir is of particular interest because of its high melting point and high corrosion resistance. In addition, since Ir and Ni both have fcc structure and they form a complete solid solution system, a high amount of Ir is expected to be alloyed to Ni-based superalloys without destroying phase stability. This study is aimed at investigating the microscopic distribution of Ir in Ni-based single-crystal superalloys. Atom-probe field ion microscopy (APFIM) revealed that Ir atoms have a small preference to be located in the gamma phase and to substitute for the Al site in the gamma prime precipitates, which is in agreement with numerical estimations by cluster variation method (CVM) and Monte Carlo simulations (MCS). In this presentation, the distribution of other PGMs in Ni-based alloys is briefly discussed in comparison to Ir-containing alloys.

4:00 PM

The Effect of Deformation and Annealing Conditions on Recrystallization of Deformed Single Crystals and Polycrystals of Iridium: N. I. Timofeev[1]; A. V. Ermakov[1]; *S. M. Klotsman*[2]; V. G. Pushin[2]; V. N. Kaigorodov[1]; L. I. Yurchenko[2]; V. K. Rudenko[1]; A. N. Timofeev[2]; P. E. Panfilov[3]; [1]Ekaterinburg Non-Ferrous Metals Processing Plant, The Head of Rsch. Ctr., Lenin Ave. 8, Ekaterinburg 620014 Russia; [2]Institute of Metal Physics, Urals Div. of Russian Acad. of Sci., S. Kovalevskaya 18, Ekaterinburg 620219 Russia; [3]Urals State University, Lab. of Strength, Ekaterinburg 62001 Russia

The recrystallization threshold of pure (4N) single crystals of iridium was analyzed as a function of the deformation (atmosphere and temperature) and annealing (air or ultra-high vacuum) conditions. Similar to other FCC metals, primary recrystallization of iridium was observed at 0.3-0.4 T_{melt} (T_{melt}-Ir melting point) after it was deformed in a "jacket" at room temperature and annealed under a ultra-high vacuum.

4:20 PM

Microscopic Theory of Defect Structure and Peculiar Mechanical Properties of Iridium: *Yu. N. Gornostyrev*[1]; O. N. Mriasov[2]; A. J. Freeman[2]; N. I. Medvedeva[3]; M. I. Katsnelson[1]; A. V. Trefilov[4]; [1]Russian Academy of Sciences, Instit. of Met. Physics, S. Kovalevskaya 18, Ekaterinburg 620219 Russia; [2]Northwestern University, Dept. of Phys. and Astronomy, Evanston, IL 60208-3112 USA; [3]Institute of Solid State Chemistry, Pervomaiskaya str. 91, Ekaterinburg 620219 Russia; [4]Kurchatov Institute, Russian Sci. Ctr., Kurchatov Sq., Moscow 123182 Russia

The brittle failure after a long stage of plastic deformation is the most surprising feature in mechanical properties of Ir and its analog, Rh, separating them from other FCC metals. On the base of ab initio total energy calculations, the peculiarities of the structure and energetic characteristics of defects in Ir (vacancies, dislocation, stacking faults) and cleavage decohesion process are investigated. We have carried out corresponding calculation also for Au which is an example of an FCC metal with a typically ductile behavior. Comparing the dislocation and vacancy formation characteristics (scalable by such factors as melting temperature, or FCC metals). A distinguishing feature of Ir is a relatively small decohesion energy (in comparison with elastic moduli) which leads to its brittle fracture, according to standard Rice-Thomson criteria of brittle-ductile behavior. The reason of this is a peculiar character of chemical bonding which is very strong for small displacements due to ion overlap butdiminishes rapidly with increased distance.

4:40 PM

About Martensitic Transformation in ZrIr Compound: *Yu V. Kudryavtsev*[1]; E. L. Semenova[2]; [1]Institute of Metal Physics, Acad. of Sci. of Ukraine, Vernadsky str., Kiev 252142 Ukraine; [2]I.N. Frantsevich Institute for Problems of Material Science, Acad. of Sci. of Ukraine, Krzhyzhanovsky str., Kiev 252180 Ukraine

There is some controversy as to crystal structure and nature of martensitic transformation (MT) in the equiatomic compound ZrIr. The latter is known to relate to the class of compounds formed as a result of interaction between transition metals of IV and VIII groups and to reveal transformation in solid similar to that in TiNi. Crystal structure of high-temperature modification of ZrIr was previously reported to be cubic B2-type (at 1050°C) and of low-temperature modification-a monoclinic B19-type (at room temperature). The transformation in ZrIr was recorded by means of X-ray, microstructure, electric resistivity, and differential thermal analysis methods. Shape memory effect (SME) for ZrIr was predicted by analogy with ZrRh and TiNi. An attempt to reveal SME in ZrIr was previously undertaken but failed. The martensitic phase of ZrIr was identified as a stacking variant of CrB-type structure. The current report presents new finding of our study carried out with aim to make clear when the SME would be displayed in ZrIr. The heating and cooling of ZrIr specimen were conducted in two regimes. By the first, speed of cooling and heating was quite low, about 10°/min. The five cycles (heating up to temperature above A_f, ~940°C, loading, cooling under the load down to temperature below M_f, 710°C, unloading, heating again up above A_f) were fulfilled and in each of them the specimen was bent on cooling substantially but did not reveal the shape restoration on heating. The lack of SME in ZrIr as compared to ZrRh (in spite of isostructurality in both origin and martensitic phases, similarity of shape of both electric resistivity and thermal curves) was suggested to be due to increased diffusion processes at higher temperatures. To inhibit diffusion processes in ZrIr, a specimen heating rate of about 100°/scc was used. In this case, the shape restoration in ZrIr of about 71-75% was observed. The possibility of the restoration degree increase in ZrIr as well as the divergence of our data on crystal structure of the ZrIr martensitic phase is discussed.

5:00 PM

Characteristic Features of High Temperature Properties of Iridium Among FCC Metals: M. I. Katnelson[1]; A. V. Trefilov[2]; K. Yu. Khoromov[2]; A. Yu. Rumyantsev[2]; *Yu. N. Gornostyrev*[1]; [1]Institute of Metal Physics, Urals Brnch. Russian Acad. of Sci., Ekaterinburg 620219 Russia; [2]Kurchatov Institute Russian Science Center, Moscow 123182 Russia

The dispersion in the entire Brillouin zone and the temperature dependence (right up to the melting temperature) of the anharmonic frequency shift and phonon damping in a number of FCC metals is investigated on the basis of microscopic calculations. It is found that the anharmonic effects depend sharply on the wave vector in the directions of the G-X, X-W, and G -L and, in contrast to BCC metals, the magnitude of the effects is not due to the softness of the initial phonon spectrum. It is shown that the relative frequency shifts and the phonon damping near melting do not exceed 10-20%. The relative role of various anharmonic processes is examined, and the relation between the results obtained and existing experimental data is discussed.

Kleppa Symposium on High Temperature Thermochemistry of Materials: Session II

Sponsored by: ASM International: Materials Science Critical Technology Sector, Extraction & Processing Division, Thermodynamics & Phase Equilibria Committee, Process Fundamentals Committee

Program Organizers: Ray Y. Lin, University of Cincinnati, Department of Materials Science and Engineering, Cincinnati, OH 45221-0012 USA; Y. Austin Chang, University of Wisconsin, Department of Materials Science & Engineering, Madison, WI 53706-1595 USA; Dr. Susan Meschel, The University of Chicago, Chicago, IL 60637 USA; Ramana Reddy, University of Alabama, Department of Metals and Materials Engineering, Tuscaloosa, AL 35487 USA

Monday PM — Room: Lincoln E
March 13, 2000 — Location: Opryland Convention Center

Session Chairs: Y. Austin Chang, University of Wisconsin, Dept. of Matls. Sci. & Eng., Madison, WI 53706-1595 USA; Robert J. Gottschall, US Department of Energy, Germantown, MD 20874-1207 USA

2:00 PM

Enthalpies of Formation of NiAl and Compounds in the Al-Ni-Y System: *Philip Nash*[1]; Ole Kleppa[2]; [1]IIT, Mmae Dept., 10 W. 32nd St., Chicago, IL 60616 USA; [2]University of Chicago, James Frank Instit., S. Ellis Ave., Chicago, IL USA

The enthalpy of formation of NiAl as a function of composition has been determined by high temperature reaction calorimetry. The value for the Ni0.5A10.5 composition is -61.0±1.1 kJ/mole. The enthalpies of formation of the ternary compounds All6Ni3Y, Al4NiY, and A12NiY and of the binary compound A12Y containing nickel have also been measured. The enthalpy values measured are compared to previously published results where available.

2:30 PM

High Temperature Calorimetry in Solid-Gas Reactions: Application to the Intermetallic Hydride Compounds: *P. Dantzer*[1]; [1]Universite de Paris-Sud, Cnrs Umr 8647, Bat 415, Orsay, Cedex 91405 France

In order to study the intermetallic compounds-H_2 systems, one has to consider the problems created by the presence of a powdered activated sample and the manifestation of hysteresis during the formation-decomposition of the hydrides. Due to the low thermal conductivity of the powder, strong non isothermal behaviors can lead to strong temperature gradients within the sample, which in turn may induce metallic diffusion and disproportionation of the compound. Hysteresis implies a non reversible character of the solid phase transformation and the possibility of describing different thermodynamic paths during the scan of the hysteresis loops. Solutions to these problems have been brought by a sharp control of the thermodynamic variables during the phase transformation. Thus to maintain quasi-isothermal conditions, a reliable control of the temperature inside the sample is insured by optimizing the hydrogen gas flow rate. The measurements have been carried out with an automatic apparatus, consisting of a heat flow calorimeter coupled with high precision volumetric devices. It provides accurate characterizations of the thermodynamic properties as well as informations of the dynamic aspects of the hydride phase growth, over a wide range of pressures 0-4 MPa and temperatures 250-800 K. The ensemble constitutes a closed system in which high purity hydrogen gas is permanently transferred between hydrides reservoirs and reactors with high thermal transfer capacity. The excellent stability of the signal of the calorimeter, ±4nV over a long period of time (>10 days), allows to measure directly the heat evolved during the scan of an hysteresis loop, with an average accuracy of 1%. Kinetic of the phase transformation is based on the analysis of the measured heat flux, where the true rate law at the sample level is obtained by deconvoluting the measured signal. It is shown that only overall informations can be expected; the results of the numerical treatment raise the problem of the location of the heater used for calibration of the calorimeter. Investigations have been carried out with the ZrNi-H_2 system.

3:00 PM

Calorimetric Study on Hydration of CaO-Based Oxides: *Yasutaka Iguchi*[1]; Takayuki Narushima[2]; Chihiro Izumi[3]; [1]Tohoku University, New Industry Creation Hatchery Ctr., Arakaki Aza Aoba, Aoba-ku, Sendai 980-8579 Japan; [2]Tohoku University, Dept. of Metallu., Aramaki Aza Aoba, Aoba-ku, Sendai 980-8579 Japan; [3]Tohoku University, Grad. Schl., Aramaki Aza Aoba, Aoba-ku, Sendai 980-8579 Japan

Weathering disintegration of steelmaking slag is caused by volume expansion due to the hydration of free-CaO and CaO-based materials in the slag. In the present work, heat of hydration of CaO solid solutions (CaO-MnO and CaO-FeO systems) and CaO compound oxides were measured by a solution calorimetric technique and the relationship between the heat of hydration and expansion due to hydration was clarified for these materials. The heat of hydration was evaluated with enthalpy change of a reaction with distilled water at 327K, and the expansion was determined in an argon-water vapor atmosphere at 353K. Effects of MnO and FeO contents in the solid solution on heat of hydration or expansion were shown. The difference of expansion rates for CaO compound oxides was discussed from the point of view of hydration products.

3:30 PM

The Standard Enthalpies of Formation of the Compounds of Early Transition Metals with Late Transition Metals and with Noble Metals as Determined by Kleppa and Co-Workers at the University of Chicago-A Review: *Qiti Guo*[1]; [1]University of Chicago, James Franck Instit., 5640 S. Ellis Ave., Chicago, IL USA

Since the early 1980's, experimental studies of the standard enthalpies of formation of the binary intermetallic compounds of early transition metals with late transition metals and with noble metals have been a major long-term research project in this laboratory. Tabulated in this review are 265 enthalpy of formation values for 252 such compounds, all determined in this laboratory during the last two decades. The calorimetric methods used in these investigations have included solution calorimetry, solute-solvent drop calorimetry, and direct synthesis calorimetry. Among these methods the direct synthesis approach has been the most frequently used technique. In this review our results will be compared with values published by other laboratories and with values predicted by the Miedema semi-empirical model. However, the emphasis will be placed on the systematic variation of the standard enthalpy of formation for some characteristic alloy families from group to group in the periodic table. A few examples will be presented to show the correlation between the enthalpy of formation and the pertinent atomic number in the binary alloy families.

4:00 PM Break

4:10 PM

Analysis of the Enthalpy of Mixing Data of Binary and Ternary (Rare Earth (Nb, La, Y, Yb)-Alkali Metal) Halides Systems: *Marcelle Gaune Escard*[1]; Michael Hoch[2]; [1]Universite de Provence, IustiI-Cnrs Umr 139, Technopole de Chateau Gombert, 5 rue Enrico Fermi, Marseille, Cedex 13 13453 France; [2]University of Cincinnati, Dept. of Matls. Sci. and Eng., Cincinnati, OH 45221-0012 USA

We analyzed the enthalpy of mixing data of several liquid Rare Earth–Alkali metal halides using the Hoch-Arpshofen solution model. We investigated the $NdCl_3$-MCl (M is Na, K, Rb, Cs,), $NdBr_3$-MB_r (M is Li, Na, K, Rb, Cs), $LaBr_3$-MBr (M is Li, Na, K, Rb, Cs), (LaF_3, YF_3, YbF_3)-MF (M is Li, Na, K, Rb, Cs)" binary systems, and the ternary $NdCl_3$-LiCl-KCl, LaF_3-NaF-LiF systems in the binary systems the larger the M+ radius, the larger the maximum (in absolute terms) of the

enthalpy of mixing. Larger the anion radius L- the smaller the maximum of the enthalpy of mixing. In the binary systems NdL3-ML the maximum of the enthalpy of mixing is given by the equation: Hm max (in kK) =-(2.392± 0.165)*r_M+ +(0.742±0.112) *r_{L-}. In the binary systems LaL_3-ML the maximum of the enthalpy of minimum is given by the equation: Hm max (in kK) +- (2.029±0.179)*r_M+ +(0.642±0.133)*r_{L-}. In the ternary system $NdCl_3$-LiCl-KCl along the line $NdCl_3$-(0.58 LiCl + 0.42 KCl) the enthalpy of mixing equals that of NdCl3-NaCl, because the weighted average radius of (0.58 Li+ + 0.42 K^+) equals that of Na^+. In the ternary system LaF_3-NaF-LiF the enthalpy of mixing could be computed from the binary systems. The composition of the maximum of the enthalpy of mixing depends on the radius of the rare earth and anion. If the rare earth radius is large compared to the anion radius (La vs F) the maximum is at x_{MF}+ 0.5. if the rare earth radius is smaller, (Dy vs Cl) the maximum shifts to ^xM_V + 0.69.

4:40 PM

Enthalpies of Mixing in Fe-C-Si Melts: *Mark E. Schlesinger*[1]; Qinfang Xiang[1]; [1]University of Missouri-Rolla, Dept. of Metallu. Eng., 1870 Miner Circle, Rolla, MO 65409-0340 USA

The accuracy of mass and energy balance calculations in iron- and steelmaking is highly dependent on the enthalpy of mixing of molten iron-based solutions, in particular Fe-C-Si melts. These enthalpies of mixing are difficult to determine experimentally, and as a result are calculated using a variety of models derived from Gibbs energy of mixing data. A comparison of calculated enthalpies of mixing in the Fe-C-Si ternary system is made, using several different modeling approaches. Featured modeling methods include the regular-solution model of Schmid and Wagner's model for multicomponent dilute solutions. The modeling results are compared with experimental data reported by Vitusevich et al.

5:10 PM

Thermochemical Study on Stability of Zro² Fine Particles: *T. Mitsuhahsi*[1]; [1]National Institute for Research in Inorganic Materials, 1-1 Namiki, Tsukuba, Ibaraki 305-0044 Japan

It is well known that high-temperature tetragonal Zro² with fine particle sizes occurs even at room temperature. Though this problem has been discussed from both views of kinetics and thermodynamics, a clear explanation has not been made. A high-temperature solution calorimetry may give the clear answer under consideration of heat capacity. In the present work, some of tetragonal and monoclinic fine particles were prepared. A Calvet twin micro-calorimeter was used to measure heats of solution of samples into a solvent. The sample powders were dropped from 298K into $3Na_20_4MoO_3$ solvent at 970K. Heat capacities were measured from 298K to 900K by DSC method. Measurements of heats of solution gave the values of 9.5 to 18 kJ/mol for t-Zro² and 21 to 29 kJ/mol for mZro², respectively. By considering surface areas and strain in particles, enthalpy of transition and surface energy difference between t- and m-Zro² were estimated to -12.5kJ/mol and 0.1J/m² at 298K, respectively. It is clearly concluded under consideration of heat capacity data that t-Zro² fine particles are thermodynamically unstable below 700K, compared with m-Zro² fine particles.

5:40 PM

Spinal Oxide Calorimetry: *M. Wakihara*

Abstract text is unavailable

Magnesium Technology 2000: Thermal Reduction and Environmental Issues

Sponsored by: Light Metals Division, Reactive Metals Committee, International Magnesium Association

Program Organizers: Howard I. Kaplan, Magnesium Corporation of America, Salt Lake City, UT 84116 USA; John N. Hryn, Argonne National Laboratory, Argonne, IL 60439-4815 USA; Byron B. Clow, International Magnesium Association, McLean, VA 22101 USA

Monday PM — Room: Bayou C
March 13, 2000 — Location: Opryland Convention Center

Session Chair: John N. Hryn, Argonne National Laboratory, Argonne, IL 60439 USA

2:00 PM

Fundamentals of Serpentine Leaching in Hydrochloric Acid Media: *J. E. Dutrizac*[1]; T. T. Chen[1]; C. W. White[2]; [1]CANMET, 55 Booth St., Ottawa, Ontario K1A0G1 Canada; [2]Metallurgie Magnola Inc., 620 Rene Levesque W., Montreal, Quebec H3B1N7 Canada

In the Magnola process, magnesium metal is produced by the electrolysis of anhydrous MgCl2 derived from the leaching of serpentine, which is the major constituent (>90%) of asbestos tailings. Serpentine reacts rapidly in concentrated HCl media, and the leaching rate is essentially independent of the rotation speed of disks of the massive mineral. The implication is that the rate is chemically controlled, and this conclusion is supported by the moderately high temperature dependence and the approx. 40 kJ/mol apparent activation energy. At 95°C, the leaching rate of the asbestos tailings increases as the 0.5 power of the HCl concentration, but is independent of the concentrations of FeCl3 or FeCl2, for concentrations as high as 1.0 M of either salt. The accumulation of the MgCl2 reaction product in the leaching solution suppresses the leaching rate, and high total chloride concentrations result in the "boiling" of HCl from the solution. The leaching reaction occurs over a diffuse reaction zone up to 400 µm thick. As a consequence, the leaching rate is nearly independent of the particle size for serpentine particles less than 600-800 µm in diameter. The implication is that fine grinding of the asbestos tailings is not required. The leaching reaction generates soluble magnesium and an amorphous silica reaction product. In acid media, only trace silica dissolution occurs; virtually all of the silica forms an insoluble psuedomorph after the original serpentine.

2:25 PM

Reduction of Molten MgO-Bearing Slags with Ferroaluminium: *José Deodoro Trani Capocchi*[1]; V. Rajakumar[2]; [1]University of São Paulo, Dept. of Metallu. and Matls. Eng., Polytech. Schl., Av. Prof. Mello Moraes, 2463, São Paulo, SP 05508-900 Brazil; [2]CSIRO Minerals, Light Met. Product., Clayton, Vic 3172 Australia

Molten slags of the composition 5.6% MgO, 48.1% Al2O3 and 46.3% CaO were reacted with ferroaluminium (80% Al and 35% Al), in graphite crucibles, at 1435-1450°C and reduced pressure 3,066.36-8,399.16 Pa(23-63mmHg). A technique was developed for measuring the rate of evolution of magnesium vapour transported from the reaction zone to a condenser, which was continuously weighted by means of a load cell. It was found that, in the range of operating pressures and composition studied the final yield of magnesium increased linearly as the pressure decreased. The rate per unit driving force with the 80% Al-alloy was 4.7 times that with the 35% Al-alloy mainly because of the larger slag/metal interfacial area when the 80% Al-alloy was used. The overall process appears to be controlled by transport in the slag phase and/or a first order reversible reaction taking place at the slag/metal interface.

2:50 PM

Magnesium Metal by the Heggie-Iolaire Process: *Michael W. Wadsley*[1]; [1]Austherm Pty Limited, P.O. Box 2049, North Brighton, Victoria 3186 Australia

The Heggie-Iolaire Process involves the ambient pressure aluminothermic reduction of magnesia derived from magnesite and dolomite in a thermal plasma arc furnace using selected sources of scrap aluminium. Test work has been conducted at the scale of 2.5 kg/hr and 10 kg/hr magnesium metal production rates. This paper presents some of the results of this test work and of process modeling. A comparison is made between this process and published information concerning other methods for the metallothermic production of magnesium metal. The factors affecting the recovery of liquid metal from its vapour are discussed. A comparison is made between the condensation of magnesium metal and published information for the commercial recovery of liquid zinc metal from its vapour.

3:15 PM

Protective Atmospheres for the Heat Treatment of Magnesium Alloys: *P. F. Stratton*[1]; E. K. Chang[1]; [1]BOC Gases, European Dev. Ctr., Rother Valley Way, Holbrook, Sheffield S203RP UK

Most magnesium alloys are used for die castings which, due to the presence of porous cores, cannot be heat treated at present without blistering. However, as technology improves, pore-free castings will become available whose properties can be optimised by heat treatment and environmentally friendly protective atmospheres will be required for mass production processing. The remaining sand cast magnesium-zirconium alloys, mainly used for aerospace components, are currently heat treated. The most common alloy, ZE41, is usually only treated to the T5 temper whereas the increasingly popular WE43 is treated to T6 temper. During that heat treatment there is a potential fire hazard which can be solved by the correct application of a protective atmosphere. There is always a risk of fire in any magnesium heat treatment due to equipment failure or local furnace hot spots. The risk of ignition is particularly acute for alloys which must be solution treated at over 400°C at which temperature some form of protective atmosphere has historically always been advised. The atmospheres recommended leave a great deal to be desired in terms of effective control, toxicity and environmental impact. A study of non-toxic environmentally friendly alternatives is presented for ZE41 and WE43. One route to pore-free castings is hot isostatic pressing (HIP). If HIP of magnesium castings is to become a standard process within the automotive industry, the cost must not be prohibitive. One way of reducing costs would be to replace the argon pressurisation medium with nitrogen and the effects of doing so are examined.

3:40 PM Break

3:50 PM

The Use of Sulphur Dioxide as a Cover Gas for Molten Magnesium: *S. P. Cashion*[1]; N. J. Ricketts[1]; [1]Australian Magnesium Corporation, Level 6, 9 Sherwood Rd., Toowong, Queensland 4066 Australia

The use of sulphur dioxide (SO_2) as a cover gas component for the oxidation protection of molten magnesium is a viable alternative to sulphur hexafluoride (SF6). The two major problems with SF6 are its high cost and extremely high Global Warming Potential of approximately 24,000. In comparison, SO_2 is relatively inexpensive and has a Global Warming Potential of zero. However, there has been some concern regarding the safety of SO_2, in particular its use as a cover gas in high pressure die casting furnaces. During the 1940's and 1950's, numerous incidents were reported in magnesium die casting operations, occurring in the sulphur domes used to protect the magnesium die casting alloys. This "Sulphur Dome Effect" was attributed to the formation of magnesium sulphate, resulting from the use of SO_2. An investigation was conducted into the Sulphur Dome Effect. Variables examined covered the range of processing operations generally experienced in primary magnesium production and magnesium die casting. The Sulphur Dome Effect was simulated in the laboratory under a range of operating conditions. The reaction associated with the Sulphur Dome Effect appears to occur from a reaction between an accretion on the wall of the crucible and the molten magnesium. Chemical analyses of the accretion and surface film revealed the presence of MgO and $MgSO_4$ in the surface film and the crucible scale. Highly unstable $Al_2(SO_4)3$ was also detected in the crucible scale. These findings support the current proposed mechanism. Further investigations were conducted into the use of sulphur dioxide gas mixtures in ingot and sow casting of pure magnesium and magnesium die casting alloys. The results from this study indicate that the use of SO_2 gas mixtures for the protection of molten magnesium may present a safety problem under certain operating conditions. However, for some applications, such as ingot casting of magnesium die casting alloys, dilute sulphur dioxide gas mixtures are a viable alternative to SF6.

4:15 PM

EPA's Voluntary Partnership with the Magnesium Industry for Climate Protection: *Scott Charles Bartos*[1]; [1]U.S. Environmental Protection Agency, Climate Protect. Div., 401 M St. S.W. (6202J), Washington, DC 20460 USA

The U.S. Environmental Protection Agency (EPA) develops and fosters cooperative partnerships with a wide range of industries to reduce U.S. emissions of greenhouse gases. One such voluntary partnership is the SF6 Emission Reduction Partnership for the Magnesium Industry. Started in 1998, this partnership seeks to reduce the U.S. magnesium industry's emissions of the extremely potent greenhouse gas, sulfur hexafluoride (SF6). The magnesium industry employs SF6 to prevent the rapid oxidation and burning that occurs when the molten metal directly contacts air. A continuous flow (and subsequent release) is required to maintain a protective layer of gas at the melt surface. SF6, an odorless and non-toxic gas, has been the industry standard for melt protection for more than 20 years. However, the industry has recognized that continued emission of this long-lived, extremely potent greenhouse gas is a costly and unsustainable business practice and has begun to work with EPA to reduce emissions and evaluate emission control technologies. In response to this environmental concern, EPA has launched a new initiative to assist the industry in its effort to reduce SF6 emissions. As a voluntary partner, an individual magnesium producer or casting company signs a memorandum of understanding (MOU) with EPA committing to annually report their emissions of SF6 and take cost-effective and technically feasible actions aimed at reducing those emissions. EPA works together with its industry partners to review and evaluate emission reduction strategies and technologies, promote technical information sharing by preparing annual reports and hosting technical conferences, record and verify the partner's progress, and provide positive public recognition for the partners' achievements. The MOU encourages partners to follow a pollution prevention approach to reduce SF6 emissions. This approach, as outlined in the United States Pollution Prevention Act of 1990, presents a hierarchy of emission reduction options that includes source reduction of SF6 by reducing leaks and assuring appropriate cover gas concentrations and flow rates, substitution of SF6 with a more environmentally benign chemical, capture and reuse of SF6, and lastly, destruction of the chemical before release to the environment. Many companies have already implemented various cost-effective source-reduction efforts including regular inspection and maintenance of the gas distribution system, installation of central cover gas blending equipment, and analysis of cover gas concentration and distribution at the molten metal's surface. In addition, a small group of magnesium companies are currently evaluating the technical feasibility and occupational safety concerns associated with installing either SF6 capture/recycle systems or SO_2-based alternative cover gas systems. While the casting technologies of magnesium producers are distinctly different from those of casting companies, both rely heavily on SF6 to provide crucial melt protection. Seven of the approximately forty companies that produce and cast magnesium in the U.S. have joined EPA as partners. As of June 21, 1999, the following companies have signed MOUs with EPA: Acme Die Casting, Chicago White Metal Casting, Del Mar Die Casting, Diemakers, Hyatt Die Cast & Engineering Corporation, Magnesium Products of America, Spartan Light Metal Products. Several more companies are expected to join the partnership this year.

Packaging & Soldering Technologies for Electronic Interconnects: Applications of Multicomponent Phase Equilibria in Electronic Packaging

Sponsored by: Electronic, Magnetic & Photonic Materials Division, Electronic Packaging and Interconnection Materials Committee

Program Organizers: Hareesh Mavoori, Bell Laboratories, Murray Hill, NJ 07974 USA; Srini Chada, Motorola, Plantation, FL 33322 USA; Gautam Ghosh, Northwestern University, Department of Materials Science, Evanston, IL 60208-3108 USA; Martin Weiser, AlliedSignal Electronic Materials, Plated and Discrete Products, Spokane, WA 99216 USA

Monday PM Room: Lincoln D
March 13, 2000 Location: Opryland Convention Center

Session Chairs: K.-N. Tu, University of California, Dept. of Matls. Sci. Eng., Los Angeles, CA 90095 USA; H. Mavoori, Bell Laboratories, Murray Hill, NJ 07974 USA

2:00 PM Invited
Phase Equilibria of Sn-In Base Micro-Soldering Alloys: *Kiyohito Ishida*[1]; [1]Tohoku University, Dept. of Matls. Sci., Aoba-yama 02, Aoba-ku, Sendai, Miyagi Prefecture 980-8579 Japan

We recently developed a thermodynamic database for the calculation of phase diagrams in micro-soldering alloy systems, which consists of the elements Pb, Bi, Sn, Sb, Cu, Ag and Zn. The important element In was not available at the time. In order to include In in this database, therefore, the phase equilibria of some In base alloys have been experimentally determined by DSC, EDX, X-ray diffraction, etc., and thermodynamic assessments have been made by CALPHAD method. In the present paper, the phase equilibria and thermodynamic properties of some Sn-In-X (X: Ag, Zn, Sb, Bi) ternary systems will be shown, which have practiced applications in the development of Pb-free solders with low melting temperatures.

2:25 PM
Growth of a Au-Ni-Sn Intermetallic Compound on the Solder-Substrate Interface after Aging: *Andrew Murphy Minor*[1]; John W. Morris[1]; [1]University of California, Dept. of Matls. Sci. and Min. Eng., Lawrence Berkeley Labs. Bldg. 66-200, One Cyclotron Rd., Berkeley, CA 94720 USA

When Ni/Au metallization is used to form joints with eutectic solder, the as-solidified joints have $AuSn_4$ precipitates distributed throughout the bulk, with Ni_3Sn_4 at the interface. Recent work has shown that the Au-Sn redeposits onto the interface during aging, compromising the strength of the joint. The present work shows that the redeposit is a ternary intermetallic $Au_{0.5}Ni_{0.5}Sn_4$. While this intermetallic has, to our knowledge, not been seen previously, it appears to be a ternary variant of $AuSn_4$. It does not form during the initial soldering since the solubility of Au in molten Pb-Sn solder separates the Au and Ni constituents.

2:45 PM
Formation and Migration of $AuSn_4$ in BGA Solder Joints Having the Au/Ni Surface Finish: *C. E. Ho*[1]; Y. M. Chen[1]; C. Robert Kao[1]; [1]National Central University, Dept. of Chem. Eng., Chungli, Taiwan

The Au/Ni two-layer structure is a very common surface finish for the solder-ball pads in the Ball-Grid-Array (BGA) packages. During reflow, a layer of $AuSn_4$ will form from the reaction of the Au layer with Sn in the solder. The $AuSn_4$ layer will subsequently break off and fall into the solder joints as individual $AuSn_4$ particles. In the past few years, it was found that post-reflow aging will bring these $AuSn_4$ particles back to the solder-joint/pad interface, forming a dense, continuous $AuSn_4$ layer. This $AuSn_4$ layer will break off and come back repeatedly upon further reflow-aging cycles. The mechanism for this scientifically very interesting phenomenon remains unknown. Being very brittle, the $AuSn_4$ layer will severely deteriorate the strength of a solder joint. Therefore, this phenomenon is also technologically very important. The purpose of our study is to investigate the mechanism for this phenomenon. We will present the most recent results of our study. It is believed that this phenomenon strongly correlates with the low melting point of $AuSn_4$, high diffusivity of Au in solder, and the phase relationships in the Au-Ni-Sn ternary system.

3:05 PM
Use of Multicomponent Phase Diagrams for Predicting Phase Evolution in Solder/Conductor Systems: *Kejun Zeng*[1]; Weiqun Peng[1]; Jorma Kivilahti[1]; [1]Helsinki University of Technology, Dept. Elect. and Comm. Eng., Lab. of Elect. Prod. Tech., Otakaari 5A, PL 3000, Espoo FIN-02015 Finland

Although the complete phase equilibrium is never reached in interconnection applications, the assumption of local equilibrium at the interfaces is generally valid in most systems composed of dissimilar materials. Therefore, the tie lines in ternary (or multicomponent) phase diagrams-together with the relevant stability diagrams and the mass balance requirements-can be used for predicting the phase sequences (i.e. diffusion paths) formed, for example, in solder/conductor joints. Generally, binary phase diagrams cannot provide sufficient information on the phase formation in a solder/conductor systems because they do not bear any information on the relative stabilities between different binary phases in multicomponent systems. As examples, the formation of intermetallic compounds in several solder/conductor systems with Au- or Cu-metallization was studied with the help of ternary phase diagrams as well as experimentally, demonstrating the inadequacy of the binary information. The phase diagrams were calculated by using the thermodynamic methods. The experimental results confirmed that the dependence of formation of intermetallic compounds on temperature and solder composition is clearly represented by the ternary phase diagrams supplemented with the stability diagrams.

3:25 PM Break

3:40 PM Invited
Thermodynamic Assessment of the Sn-Ag-Cu System: *U. R. Kattner*[1]; K. -W. Moon[1]; W. J. Boettinger[1]; C. A. Handwerker[1]; [1]NIST, Metallu. Div., Mail Stop 8555, Gaithersburg, MD 20899 USA

Experimental data on the Sn-Ag-Cu system will be summarized. Alloys in this system are being studied for their potential as Pb-free solders. Thus the location of the ternary eutectic involving L, Sn, Ag_3Sn and Cu_6Sn_5 phases in the Sn-rich corner is of critical interest. Thermodynamic extrapolation of the diagram from the three constituent binary systems using the CALPHAD method will be presented. A comparison to the experimental data will indicate the need for refined binary assessments and/or ternary interaction parameters. For various solder compositions, solidification paths and freezing ranges will be predicted with a Scheil analysis. These predictions will be compared to experimental solidification results obtained in this work and in the literature.

4:05 PM
Phase Equilibria and Related Properties of Sn-Ag-Cu Based Pb-free Solder Alloys: *I. Ohnuma*[1]; X. J. Liu[1]; H. Ohtani[1]; K. Ishida[1]; [1]Tohoku University, Dept. of Matls. Sci., Aoba-yama 02, Aoba-ku, Sendai, Miyagi Prefecture 980-8579 Japan

We recently developed a thermodynamic database for micro-soldering alloys which consists of the elements Pb, Bi, Sn, Sb, Cu, Ag, Zn, and In. In this paper, the phase equilibria and the related thermodynamic properties of the Sn-Ag-Cu base alloys are presented using this database. These alloy systems are promising candidates of Pb-free solders. The isothermal section diagrams of the Sn-Ag-Cu ternary system were experimentally determined by EDX, X-ray diffraction and metallographic techniques. Based on the present results as well as previous data on phase boundaries, thermodynamic assessments of this system were carried out. The isothermal and vertical section diagrams, liquidus surface, mole fractions of the phase constitution etc. have been calcu-

lated. Moreover, non-equilibrium solidification process using the Scheil model has been simulated and compared with the equilibrium solidification behavior in some Sn-Ag-Cu base alloys. In addition, the predictions of surface energy and viscosity are presented.

4:25 PM

Ag and Cu Migration Phenomena on Wire-Bonding: *Ker-Chang Hsieh*[1]; Theo Martens[2]; [1]National Sun Yat-sen University, Instit. of Matls. Sci. and Eng., Kaohsiung, Taiwan; [2]Philips Electronic Building Elements Industries Limited, Tech. Dev. Div., 10, Chin 5th Rd. N.E.P.Z., P.O. Box 35-48, Kaohsiung, Taiwan

The plastic packaged sample stored at 250°C for 588hrs and found the Au plus 1%Pd wire composition changed. The Ag and Cu atoms can migrate from the wedge bond through the wire surface and arrive the ball bond. At the same time, the Ag and Cu atoms diffuse into the gold wire itself and form a layer type structure. These migration phenomena can be explained after detailed microstructure analysis. The microstructure analysis was done by using the apparatus: Joel Superprobe JXA-8900R. The quantitative line scan analysis result included the identified phases and phase thickness. A similar line scan analysis was done on the ball bond section. The results has the similar layer structure as the wire section. There is two type of driving force for these atom migration phenomena. One is the Ag and Cu concentration gradient to drive the diffusion process. The other is the new alloy phases formation, which can reduce the free energy of this alloy system, based on the thermodynamic rules. The phases formation sequence formed on the wire or ball bond section is consistent with the equilibrium Ag-Au-Cu phase diagram. Conclusions: 1. Ag and Cu atoms can migrate on the wire surface and form new alloy phases. 2. The properties of gold wire will change under high temperature and long time conditions. 3. The diffusion rate of Cu is higher than Ag according to this study. 4. Impurity atoms in the molding compound may transport through the wire surface and reach the ball bond area causing corrosion or other degrading problems.

4:45 PM

The Tin-Rich Corner of the Copper-Magnesium-Tin Phase Diagram: *Eduardo E. Vicente*[1]; Alicia N. Alcaraz[1]; [1]Comisión Nacional de Energía Atómica, Matls. Dept., Av. del Libertador 8250, Buenos Aires 1429 Argentina

The copper-magnesium-tin ternary phase diagram was studied in the region Sn-Cu_6Sn_5-CuMgSn-Mg_2Sn. The employed experimental techniques were: optical microscopy, scanning electron microscopy, X-ray diffraction, electron-probe microanalysis and differential thermal analysis. A liquidus projection is proposed, which includes three invariant reactions: two ternary eutectics and a pseudobinary eutectic.

5:05 PM

The Tin-Rich Corner of the Copper-Tin-Zinc Phase Diagram: Alicia N. Alcaraz[1]; *Eduardo E. Vicente*[1]; Luis M. Gribaudo[1]; [1]Comisión Nacional de Energía Atómica, Matls. Dept., Av. del Libertador 8250, Buenos Aires 1429 Argentina

The copper-tin-zinc ternary phase diagram was studied in the region delimited by the tin corner and the 50 at%Sn isopleth. The employed experimental techniques were: optical microscopy, scanning electron microscopy, X-ray diffraction, electron-probe microanalysis and differential thermal analysis. A liquidus projection and a subsolidus isothermal section are presented.

Pressure Technology Applications in the Hydrometallurgy of Copper, Nickel, Cobalt and Precious Metals: Pressure Technology Applications in the Hydrometallurgy of Gold

Sponsored by: Extraction & Processing Division, Copper, Nickel, Cobalt Committee

Program Organizers: James E. Hoffmann, Hoffmann and Associates, Houston, TX 77242 USA; Norbert L. Piret, Piret & Stolberg Partners, Duisburg 47279 Germany

Monday PM — Room: Lincoln C
March 13, 2000 — Location: Opryland Convention Center

Session Chairs: Christopher A. Fleming, Lakefield Research Limited, Lakefield, Ontario K0L2H0 Canada; James E. Hoffmann, Hoffmann and Associates, Houston, TX 77242 USA

2:00 PM

A Novel Process for the Simultaneous Dissolution of Gold, Platinum Group Metals and Base Metals: *Christopher A. Fleming*[1]; C. Joe Ferron[1]; Dave B. Dreisinger[2]; P. Terry O'Kane[3]; [1]Lakefield Research Limited, 185 Concession St., P.O. Box 4300, Lakefield, Ontario K0L2H0 Canada; [2]University of British Columbia, Dept. of Met. & Matls. Eng., 309-6350 Stores Rd., Vancouver, British Columbia V6T1W5 Canada; [3]O'Kane Consultants Inc., 502-455 Granville St., Vancouver, British Columbia V6C1V2 Canada

There are many examples of ores, concentrates and other materials containing base metals (i.e. Cu,Ni,Co) as well as gold and platinum group metals PGMs in which either the distribution of base metals and PGMs is unfavorable, or their concentrations are too low, for these materials to be economically treated by conventional technology (matte smelting, acid pressure leaching, chlorination, etc.). A new hydrometallurgical process has been developed for treating these feed materials, and will be described in this paper. The process has the potential to significantly improve the economics of treating feeds containing base metals and PGMs. The main feature of the process is high temperature pressure leaching, under conditions that allow simultaneous and efficient (88 to 99%) dissolution of all the base metals and PGMs. Technology has also been developed to treat the product of the leaching process and recover the base metals and PGMs as separate saleable products.

2:30 PM

The Dissolution of Gold during the Pressure Leaching of Refractory Gold Ores in the Presence of Chloride: *Michael J. Nicol*[1]; Jim Qing Liu[1]; [1]Murdoch University, A J Parker CRC, South St., Murdoch, Western Australia 6150 Australia

Pressure oxidation is one of the preferred methods for the recovery of gold from refractory ores and concentrates. There have been several reports of the dissolution of gold during the acid pressure oxidation process and this has been attributed to the presence of chloride in the plant water or ore. This paper will describe the results of an electrochemical study of the behaviour of gold in acidic sulphate solutions containing varying amounts of chloride ions at high temperatures. It will be shown from both thermodynamic and kinetic studies that the oxidation of gold occurs as a result of the coupled anodic dissolution of the metal as the chlorocomplex ion with the cathodic reduction of ferric ions. Oxygen is not directly involved in the dissolution process. Conditions which will either minimise or maximise the dissolution of gold can be deduced from the thermodynamic and kinetic models.

3:00 PM
A Mineralogical Study of the Cyanide Leach Residues from Pressure-Oxidized Twin Creek Gold Ore: *T. T. Chen*[1]; J. E. Dutrizac[1]; G. L. Simmons[2]; [1]CANMET, 555 Booth St., Ottawa K1A0G1 Canada; [2]Newmont Mining Corporation, Englewood, CO 80112 USA

Gold in the Twin Creek ore is primarily associated with arsenian pyrite. During pressure oxidation, the sulphides are solubilized, but part of the dissolved iron reprecipitates as jarosite and as an iron sulphate-arsenate-phosphate phase. The pressure oxidation products are subjected to cyanide leaching. The cyanide leach residues consist of quartz, gypsum, bassanite, anhydrite, small amounts of jarosite, an iron-sulphate-arsenate-phosphate phase, as well as trace amounts of orthoclase, rutile, pyrite, hematite and monazite; all these particles are dispersed in a fine grained matrix of illite-muscovite. The autoclave leach residues contain a small amount of carbonaceous matter. Many gold grains are detected on the surface of the carbon particles, and these gold particles are not leached during cyanidation. The gold particles are typically 0.1-0.2 µm in size and commonly are embedded in the carbon surface or are coated with a K-Al-Si-S-O phase on the surface of the carbon. The gold grains are consistently associated with elevated CI contents (50-300 ppm Cl), and the implication is that the gold was transported to the surface of the carbon as a gold chlorocomplex. The poor gold cyanide leach recoveries, which initially occurred in the Twin Creek developmental circuit under certain operating conditions, are attributed to the presence of chloride in the feed. This leads to the formation of soluble gold chlorocomplexes in the autoclave and the subsequent sequestering of the gold on the surfaces of the carbon particles.

3:30 PM Break

3:45 PM
Alkaline and Acid Autoclaves at Barrick Gold: *Kenneth Glyndwr Thomas*[1]; *Richard Williams*[1]; [1]Barrick Gold Corporation, Operations Dept., 200 Bay St. P.O. Box 119, S. Tower Ste. 2700, Toronto, Ontario M5J 2J3 Canada

This paper reviews the alkaline and acid gold autoclaving experiences gained at Barrick Gold Corporation. Alkaline autoclaving was operational at Barrick Mercur, Utah, USA, on carbonaceous/sulphide refractory ore for eight years commencing in 1988. Acid autoclaves have been operational at Barrick Goldstrike, Nevada, USA., on sulphide refractory ore since 1990 and now process 17,500 stpd of ore through six large autoclaves. Information is presented on operating costs, materials of construction, reagent requirements and flowsheet developments that reduced capital and operating costs.

Professional Registration

Sponsored by: TMS, Young Leaders Committee, Professional Registration Committee
Program Organizers: Ned Bahtishi, Westinghouse Electric Company, Western Zirconium Plant, Ogden, UT 84404-9799 USA; David Alven, GENCORP/AEROJET, Jonesborough, TN 37659 USA

Monday PM — Room: Bayou A
March 13, 2000 — Location: Opryland Convention Center

Session Chairs: Ned Bahtishi, Westinghouse Electric Company, Commercial Nuclear Fuel, Ogden, UT 84404 USA; David A. Alven, GenCorp, Aerojet Ordnance, Jonesborough, TN 37659 USA

2:00 PM Opening Comments
Dr. Patrick Taylor, Professional Registration Committee, Chairman

2:10 PM
Metallurgical P.E.; What Do I Do and Why?: *Charles V. White*[1]; [1]Kettering University, I&MSE, 1700 W. Third Ave., Flint, MI 48504 USA

A discussion of the mechanics of getting licensed, what's on the exam, and why I need to do it? A review of the requirements to be licensed and the paper work needed and the timing will be covered. Secondly, what's on the exam (not a crib) but how the exam is prepared, what are the guidelines for the items and the test make up. Lastly, why do I want to put myself through all this pain? What are the issues with industrial employment vs. independent contractors and how these issue effect you as a professional.

2:35 PM
Professional Registration: A Higher Standard: *Christy Allen*[1]; [1]Tennessee Department of Commerce and Insurance, Legal Sect., 312 8th Ave. N., 25th Floor Tennessee Tower Bldg., Nashville, TN 37243 USA

State registration boards exist to protect the health, safety and welfare of the public. Boards accomplish this mission by ensuring that only properly qualified people become registered as professional engineers and that, once registered, they provide professional services in a manner consistent with protection of the public. Professional engineers are held to high standards of practice and rules of professional conduct; they face disciplinary action if they fail to uphold those standards. This program is a discussion of the ways in which the regulation of professional engineers, through the enforcement of rules of conduct, benefits professional engineers as well as the public.

3:00 PM Break

3:10 PM
The Registered Engineer as an Expert Witness: *J. Mike York*[1]; [1]York Engineering Services, 2107 N.W. Filmore Ave., Corvallis, OR 97330 USA

The current environment for consulting engineers working as expert witness is demanding. A 1993 Supreme Court decision has placed judges in the role of gate keepers to prevent "junk science" from being presented to the juries. These requirements, in turn, place an increasing burden on the expert witness to provide evidence as to their qualifications to testify. Professional registration provides an excellent reference to establish the individual as having met the requirements of knowledge in their designated field. Registration confirms the individual has met peer reviewed examination in one or more jurisdiction, i.e. state(s), that extend well beyond academic institution or single organization. For engineers trying to break into the expert witness field, professional registration credentials must be substituted for courtroom experience until that experience can be obtained. Professional registration is a key element in credential building for the aspiring expert witness.

3:35 PM
The Practice of Being a Professional Engineer: It's More Than Just a Stamp: *Larry M. Southwick*[1]; [1]L.M. Southwick & Associates, 992 Marion Ave., Ste. 306, Cincinnati, OH 45229 USA

A professional engineer's license is often required to certify the competence of a particular design or other document. These situations usually arise to fulfill certain legal requirements. However, many, probably even most, design and other engineering work do not require formal certification, but they always require, and deserve, a competent effort. Here is where professional registration perhaps has its greatest value: as a sign of trust in the work being performed. Many engineering and operating companies require that the lead engineers be registered, again not necessarily to autograph documents, but more as an indication of overall confidence in the staff and its work. While obtaining an engineering registration requires only several years of practice and satisfactorily passing a qualifying exam, certainly necessary and no mean achievements to be sure, practicing to that standard afterwards demands a continuing effort. This entails not only maintaining quality work, but doing so with integrity and forthrightness. The presentation will provide several examples of how being a professional engineer means more than just having a P.E. license stamp in one's kit.

4:00 PM

The P.E. License: Its Value in Industry: *Nick Gianaris*[1]; [1]Visteon, an Enterprise of Ford Motor Company, Chassis Sys., 6100 Mercury Dr., Dearborn, MI 48126 USA

Engineering is a field whose practitioners have various educational and experiential backgrounds in all industries and academe. Unlike other professional fields such as medicine and law, an engineer is not always required to be licensed to practice engineering in many industrial sectors. In this paper, the following will be presented: who is required to become licensed as an engineer today, why licensure in industry is significant for both the engineer and the company, personal experience in obtaining and using the P.E. license, and why the P.E. license will become more important in the future.

Surface Engineering in Materials Science I: Coatings/Films Synthesis and Processes (SP)-II

Sponsored by: Materials Processing and Manufacturing Division, Surface Engineering Committee

Program Organizers: Sudipta Seal, University of Central Florida, Advanced Materials Processing and Analysis Center and Mechanical, Materials and Aerospace Engineering, Orlando, FL 32816 USA; Narendra B. Dahotre, University of Tennessee Space Institute, Center for Laser Applications, Tullahoma, TN 37388 USA; Brajendra Mishra, Colorado School of Mines, Kroll Institute for Extractive Metals, Golden, CO 80401-1887 USA; John Moore, Colorado School of Mines, Department of Metallurgy and Materials Engineering, Golden, CO 80401 USA

Monday PM — Room: Canal B
March 13, 2000 — Location: Opryland Convention Center

Session Chairs: Narendra B. Dahotre, University of Tennessee Space Institute, Dept. of Matls. Sci. & Eng. Ctr. for Laser App., Tullahoma, TN 37388 USA; Enrique Lavernia, University of California Irvine, Dept. of Chem. and Biochem. Eng. and Matls. Sci., Irvine, CA 92697-2575 USA

2:00 PM

Thin Films of Magnetic Semiconductors-Transport Phenomena and Magnetic Properties: *L. J. Maksymowicz*[1]; M. Lubecka[1]; B. Cieciwa[1]; [1]University of Mining and Metallurgy, Instit. of Elect., Al. Mickiewicza 30, Kraków 30-059 Poland

Thin films of CdCr2Se4:In and CdCr2-2xIn2xSe4 were obtained by rf sputtering technique. We used the deposition device equipped with three cathode system and rotatable substrate holder. As-deposited samples are in amorphous state and have a form of multilayered structure of Cr/Cd-Cr-In-Se/Cr. Heat treatment provides uniform polycrystalline single films with the required composition. The samples belong to the class of soft magnetic materials; CdCr2Se4:In has the reentrant transition (REE), the energetic structure is modified diluting by In and CdCr2-2xIn2xSe4 is in the spin glass state. Both types of samples have potential for use as photodetectors. The maximum of photoconductivity is within the wavelength from 680nm to 840nm. It was found that the maximum of voltage sensitivity is shifted towards the infrared region when dilution levels are reduced. As far as the magnetic properties are concerned, we are classifying the type of magnetic order by determination the temperature dependence of magnetization (M) and unidirectional magnetic anisotropy field (Han) [1]. We have also determined the surface magnetic anisotropy energy constant versus temperature. It was found that two components contribute to this constant [2]. One originates from the exchange interaction term due to the lack of translation symmetry for surface spins as well as from the stray field of surface roughness. The second one comes from the demagnetizing field of close-to-surface layer with grad M. Both terms linearly decrease when temperature increased from 5 to 123K, but dominant contribution is from the first component. The work was partly supported by KBN Grant Nr 10.120.68. Literature [1] E.M. Jackson, S.B. Lio, S.M. Bhagat and M.A. Manheimer, J. Magn. Magn. Mater. 80(1989) 229. [2] L.J. Maksymowicz, M. Lubecka and R. Jablonski J. Magn.Magn.Mater. 192 (1999).

2:20 PM

Laser Surface Modification of TiAl Intermetallics: *S. A. McElroy*[1]; D. Yang[1]; R. G. Reddy[1]; [1]University of Alabama, Metallu. and Matls. Eng., P.O. Box 870202, Tuscaloosa, AL 35487-0202 USA

Surface modification of TiAl intermetallics was investigated using Nd-YAG pulse laser. Laser processed samples were characterized for their surface morphological and compositional changes using SEM, XPS and X-ray diffraction. Large cracks along the grain boundaries and surface oxide layers in the laser processed samples were observed. Oxide layers consisted of Al2O3, TiO2, TiO and absorbed O2. Aluminum enrichment in the oxidation layers of TiAl was observed.

2:40 PM

The Synthesis, Processing and Properties of Graded Thin Film/Coating: *John J. Moore*[1]; [1]Colorado School of Mines, Adv. Coat. and Surf. Eng. Lab., Golden, CO 80401-1887 USA

The paper will discuss the design, processing and the resultant properties of graded coating systems that are needed to meet specific performance criteria. Three examples of graded coating systems will be used to demonstrate the philosophy used for coating systems for (a) forming dies, (b) oxidation resistant coatings for Mo, and (c) glass molding dies, as used in the current research programs in the Advanced Coatings and Surface Engineering Laboratory at the Colorado School of Mines.

3:00 PM Break

3:15 PM

Indium Oxide Thin Film with a Large Surface Area: *T. Pisarkiewicz*[1]; T. Stapinski[1]; A. Sutor[1]; K. Zakrzewska[1]; [1]University of Mining and Metallurgy, Dept. of Elect., Al. Mickiewicza 30, Krakow 30-059 Poland

Indium oxide (In2O3) is known as one of the gas sensing materials and then the films with a high surface-to-volume ratio are promising candidates for gas sensors. The authors deposited the films by rheotaxial growth and thermal oxidation (RGTO) technique. This technology is a two-step process in which the first step is the deposition of metallic indium onto substrates heated above the melting temperature of In and in the second step the metallic droplets are thermally oxidized in air forming the polyctystallline film. Optical reflection with the help of hemispherical attachment were performed enabling determination of light scattering. Electrical transport (conductivity, Hall effect) measured in varying gas atmosphere and temperature indicate the essential role of thin film surface in the interaction of semiconductor with the ambient gas.

3:35 PM

Si-N Coating by Plasma CVD Method: *Y. Sato*[1]; S. Ohtani[1]; N. Iwamoto[1]; [1]Ion Engineering Research Institute Corporation, 2-8-1, Tsuda-yamate, Hirakata, Osaka 573-0128 Japan

Si-N coating on steel by plasma CVD method was investigated to improve mechanical properties as hard coating. Application of pulsed DC was used for plasma formation. SiCl4 was used for silicon source. Nitrogen gas and ammonia gas were used for nitrogen source and effects of gas species on properties of films was investigated. In the case of nitrogen gas coating, nitrogen contents in Si-N films were increased with the increment of pulsed DC power up to 30at% at 2.0kW. Nitrogen contents in films coated with ammonia gas were also increased with the increment of DC power up to 50at%, which approached stoichiometry of stable silicon nitride. All of obtained Si-N coating films were formed in amorphous structure. Si2p peaks at 99.5eV (Si-Si bond) and 101.6eV (Si-N bond) were appeared with 30at% nitrogen containing films by XPS measurement. Coating with 50at% nitrogen content showed only one peak at 101.6eV. These results show that

more Si-Si bond was included in low nitrogen containing film and high nitrogen content film consist of Si-N bond. Hardness of Si-N film was changed with variation of applied DC power. The maximum hardness of HV1800 was obtained at 0.5kW DC power.

3:55 PM

Selective Area Laser Surface Alloying of Mild Steel with Carbon: *V. Sinha*[1]; G. L. Goswami[2]; G. B. Kale[2]; I. Manna[3]; [1]Ohio State University, Dept. of Matls. Sci. and Eng., Columbus, OH 43210 USA; [2]BARC, Atomic Fuels Div., Trombay, Mumbai 400085 India; [3]I. I. T., Kharagpur, Dept. of Metallu. and Matls. Eng., Kharagpur, WB 721302 India

Carburizing is an age old surface engineering technique to enhance hardness and wear resistance of steel. However, carburizing exposes the entire component to a complex heat treatment schedule and possesses several limitations in precision, energy/time economy and degree of improvement. The present study concerns laser surface alloying (LSA) with a pre-deposited carbon coating for selective area hardening of steel components without affecting the entire bulk. Rectangular specimens of 0.2% C steel were coated with 40 and 90 mm thick (d) carbon deposited by physical vapor deposition and irradiated with a 300 W Nd-YAG pulsed laser with output energy (E) = 6-12 J and pulsed duration (t) = 8-14 ms, respectively. LSA with an optimum conditions develop a predominantly martensitic microstructure with a very high (750-1000 VHN) microhardness. However, an increase in d, t and/or E leads to a higher w with a greater volume fraction of retained austenite in the microstructure and a lower hardness in the near surface region. Finally, an attempt has been made to correlate the microstructure, composition and hardness of the AZ with the LSA parameters.

4:15 PM

Synthesis of Nanocrystalline Diamond Thin Films by Chemical Vapor Depositions: *D. Zhou*[1]; A. Hussian[1]; L. Chow[2]; [1]University of Central Florida, Adv. Matls. Process. and Analy. Ctr., Dept. of Mech., Matls., and Aero. Eng., Eng. 381, Orlando, FL 32816 USA; [2]University of Central Florida, Dept. of Physics, Orlando, FL 32816 USA

Polycrystalline diamond films whose microstructures typically consist of crystallites with sizes on the order of nanometers have been successfully synthesized by a hot filament chemical vapor deposition (CVD) technique. Mixtures of methane, hydrogen, and argon were used as the reactant gases for the CVD processing, and the substrate (Si) temperatures ranged from 450 to 800°C. X-ray diffraction, transmission electron microscopy, and electron energy loss spectroscopy characterizations show the films consist of a pure crystalline diamond phase with grain sizes ranging from 10 to 30 nm. Scanning electron and atomic force microscopies analyses demonstrate that the surface of the nanocrystalline diamond films remain smooth and independent of the film thicknesses. The growth morphology of the diamond coatings, particularly the transition from microcrystalline to nanocrystalline diamonds, has been discussed in the light of the functions of the atomic hydrogen and the secondary nucleation, which are strongly affected by the hot filament CVD processing parameters. Furthermore, the potential applications of the nanocrystalline diamond thin films, such as electron field emitters, diffusion barriers, and protective coatings have been addressed.

4:35 PM

Preparation and Properties of Mo/CIS/CdS Thin Film Interfaces for Photovoltaic Applications: *S. R. Kumar*[1]; [1]National Institute of Foundry and Forge Technology, Dept. of Matls. and Metallu. Eng., Ranchi, Bihar 834 003 India

Copper indium selenide (CIS) thin film solar cells can be prepared by electrodeposition, dip coating and flash annealing at 400°C. The CIS thin films were prepared by single step electrodeposition process on molybdenum substrate potentiostatically or galvanostatically. The as deposited films are crystalline and are preferably oriented along (112) direction have low resistivity which in turn is further reduced by annealing in air. The cadmium sulphide films were prepared by dip coating technique on glass, as well as on molybdenum and CIS thin film substrates. The as deposited films are highly resistive and oriented along (002) direction. The resistivity is considerably reduced and crystallinity increases by flash annealing at 500°C. The X-ray diffractogram of the CIS thin film solar cell shows the crystalline and single phase orientation. The SEM analysis indicates well connected spherical grains which are densely packed. The I-V characteristics of the films are forward and reverse biasing is similar to the ideal diode. The open circuit voltage Voc and short circuit current density Jsc are respectively 100 mV and 5 mA/cm2. The results are preliminary in nature and by optimizing the growth conditions further improvement in the results are expected.

Teaching Electronic, Magnetic and Optical Materials: A Symposium in Memory of Professor Gregory E. Stillman: Session II

Sponsored by: Electronic, Magnetic & Photonic Materials Division, Education Committee

Program Organizer: Mark A. Palmer, Virginia Commonwealth University, Richmond, VA 23284-3015 USA

Monday PM — Room: Bayou D
March 13, 2000 — Location: Opryland Convention Center

Session Chair: Mark A. Palmer, Virginia Commonwealth University, Richmond, VA 23284-3015 USA

2:00 PM Invited

Linking Mathematics to Materials Science Through Interactive Visualization: *Shannon Pixley*[1]; Krishna Rajan[1]; [1]Rensselaer Polytechnic Institute, Depts. of Comp. Sci., Matls. Sci., and Eng., Troy, NY 12180-3590 USA

A number of mathematical manipulation skills are needed in many materials science courses. In this project, we are developing interactive computer applets teaching linear algebra principles in the context of crystallographic applications. The modules are designed to provide a direct relationship between specific skill building exercises, such as matrix manipulation, to a materials science topic. A series of applets have been built permitting the student to visualize graphically the crystallographic perspectives of specific matrix operations. This project is part of a larger effort known as Project Links, providing teaching tools in mathematics for application in a variety of engineering subjects.

2:30 PM Invited

Laboratory Experiences in Electronic Materials at the University of Michigan: *Rachel S. Goldman*[1]; [1]University of Michigan, Dept. of Matls. Sci. and Eng., Ann Arbor, MI 48109-2136 USA

We are developing a series of laboratory modules in electronic materials and have started to incorporate these into our undergraduate curriculum at the University of Michigan. Example modules include: (a) resistivity vs. temperature of metals, semiconductors, and insulators, (b) Hall effect measurements, (c) current-voltage measurements of solar cells, (d) scanning tunneling microscopy, and (e) atomic force microscopy. In this talk, I will discuss the new laboratory modules we have begun to incorporate into our junior level laboratory courses. I will also discuss some of our future plans which include the addition of magnetization and measurements of ferromagnetic materials.

3:00 PM Invited

Multidisciplinary Program in Sensor Materials and Devices: *Sheikh Akbar*[1]; Prabir Dutta[1]; Marc Madou[1]; Bruce Patton[1]; Yunzhi Wang[1]; [1]The Ohio State University, Ctr. for Indust. Sens. and Measure., 291 Watts Hall, 2041 College Rd., Columbus, OH 43210 USA

Under the umbrella of the NSF Center for Industrial Sensors and Measurement (CISM), a research and development program for harsh environment sensors is being actively pursued at Ohio State University. Research teams include students and faculty from Departments of Chemistry, Physics, Materials Science and Engineering, and Electrical,

Chemical and Mechanical Engineering. The CISM model has enriched engineering and physical science interdisciplinary education and has allowed us to develop a multidisciplinary industry-oriented curriculum that is currently being funded by the NSF-CRCD program and OSU Honors House. Under this program, a new three-course sequence (9 credit hours) in sensor materials including instructional laboratories with industrial experience is currently being developed. The courses are being designed around the multidisciplinary approach of CISM, and are being team-taught by faculty members from a wide range of disciplines. These courses are targeted for senior undergraduate and beginning graduate students. The first course covering basic scientific principles of sensor materials has already been offered once during the Spring quarter of 1999. The second course will cover different sensor applications and related technological issues. Both courses have a laboratory component. The third course will be group projects with participating industries. Group projects will target specific industries, identify a sensor need, develop a prototype and perform field-tests at the industrial site. Each project will be a team effort involving multiple students working in close collaboration with a faculty advisor and an industry co-adviser. Students entering the courses will have the appropriate background in science and engineering. Students taking this sequence along with 11 credit hours of relevant courses in participating departments including Business and Law will have the option to receive a minor or certificate degree in "Sensors and Measurements."

Ultrafine Grained Materials: Fundamentals and Process Mechanisms: II

Sponsored by: Materials Processing and Manufacturing Division, Powder Metallurgy Committee, Shaping and Forming Committee

Program Organizers: Rajiv S. Mishra, University of Missouri, Metallurgical Engineering, Rolla, MO 65409-0340 USA; S. L. Semiatin, Wright Laboratory, Materials Directorate, Dayton, OH 45440 USA; C. Suryanarayana, Colorado School of Mines, Department of Metal and Materials Engineering, Golden, CO 80401 USA; Naresh Thadhani, Georgia Institute of Technology, School of Materials Science and Engineering, Atlanta, GA 30332-0245 USA

Monday PM — Room: Polk A/B
March 13, 2000 — Location: Opryland Convention Center

Session Chair: C. Suryanarayana, Dept. of Metallu. and Matls. Eng., Golden, CO 80401 USA

2:00 PM Invited

Role of Water in Energetics of Zeolites and Layered Materials: *Alexandra Navrotsky*[1]; [1]University of California, Dept. of Chem. Eng. and Matls. Sci., Thermochemistry Facility, Davis, CA 95616 USA

The UC Davis Thermochemistry Facility has been studying the enthalpies of formation of zeolites, octahedral molecular sieves, and layered materials by a combination of high temperature reaction calorimetric techniques. We find several common trends. Dehydrated frameworks are metastable with respect to dense phases by 5-15 kJ/mol but hydrated frameworks are energetically stable by a similar amount (referred to liquid water and a 2-oxygen framework formula unit). This energetic stabilization is counterbalanced by a negative entropy of hydration. The ΔH and ΔS terms scale with each other. Thus the localization of water within the cage or layer is a major driving force in the formation of both framework and layered materials. New thermochemical data for a variety of zeolites and manganese oxide based nanomaterials will be reviewed in the context of hydration energetics.

2:25 PM Invited

Thermal Spraying of Nano-Composite Coatings: *E. J. Lavernia*[1]; R. Rodriguez[1]; M. Ice[1]; M. L. Lau[1]; [1]University of California, Dept. of Chem. and Biochem. Eng. and Matls. Sci., Irvine, CA 92697-2575 USA

Recent advancements developed in the thermal spraying of nanocrystalline materials have attracted scientific and industrial interest. Due to the relatively short dwell time of the powder particles during the thermal spray process and their inherent thermal stability, the feedstock powders are able to preserve the unique property of nanocrystalline materials in the as-sprayed coatings. The use of nanocermet powders such as WC-Co has produced coatings with increased microhardness while maintaining toughness values as compared to conventional coatings. In the present study, nano-composite Al coatings were produced by plasma spraying. The feedstock nanocrystalline powders were synthesized by mechanical milling of gas atomized 3003-Al powders with the addition of 10 vol.% SiC in liquid nitrogen for 8 hrs to produce agglomerates with increased surface area. The cryomilled powders were thermally sprayed by vacuum plasma spraying to produce Al-composite coatings. The residual stress of the nano-composite coating will be determined by X-ray diffraction analysis and compare to that of the conventional coating. The results will be rationalized based on the microstructural features observed in the transmission electron microscopy and scanning electron microscopy analyses. In addition, coating properties were characterized by microhardness and wear measurements performed on the coating cross sections and compared to those of the conventional Al-SiC coating.

2:50 PM Invited

A Cost-Effective Way to Make Nanostructured Carbides and Nitrides: *Leon L. Shaw*[1]; [1]University of Connecticut, Dept. of Metallu. and Matls. Eng., Storrs, CT 06269 USA

The time and energy needed to make nanostructured or conventional carbide and nitride powders for sintered components, such as valves, seals and bearings, could be cut to a fraction of what is now needed through a novel process developed recently at the University of Connecticut. The new process combines thermal and mechanical activation to enhance the reaction of compound formation. The basic form of the new process is to mechanically activate the reactants at room temperature through high energy milling, followed by completing the synthesis reaction at high temperatures. High energy milling at room temperature has substantially increased the reactivity of the reactants and dramatically reduced the final reaction temperature and time. The enhanced reaction has been attributed to the structural and energy state changes of the reactants caused by the mechanical treatment prior to the reaction. These structural and energy state changes contribute to the enhanced reduction through the increased reaction kinetics as well as the increased reaction driving force. Examples to illustrate these underlying mechanisms will be presented.

3:15 PM

Synthesis of Fe-TiN Composites by Thermal Plasma Processing: *Sutham Niyomwas*[1]; Banqiu Wu[1]; Ramana G. Reddy[1]; [1]The University of Alabama, Dept. of Metallu. and Matls. Eng., P.O. Box 870202, Tuscaloosa, AL 35487-0202 USA

The Fe-TiN composite was synthesized in a non-transferred arc d.c. plasma reactor from ilmenite ore concentrate using methane and ammonia as the reactive gases. The standard Gibbs energy minimization method was used to calculate the equilibrium composition of reaction species. The products were characterized by X-ray diffraction and SEM. Effect of plasma power, gas composition, ilmenite particle size, feeding rate and particle injection position on purity of composite were investigated. Experimental and theoretical results were discussed.

3:35 PM

Activated Sintering of Al_2TiO_5 Nanoceramics: *Joanna Groza*[1]; Vladimir Kodash[1]; Lia Stanciu[2]; Maria Zaharescu[2]; [1]University of California, Chem. Eng. Matls. Sci., One Shields Ave., Davis, CA 95616 USA; [2]Institute of Physical Chemistry-Romanian Academy, Bucharest, Romania

The most critical stage in obtaining nanoceramics is sintering. Key to success is preserving the nanocrystalline size of starting powders in final consolidated ceramics. One way to achieve this objective is by sintering activation using an externally applied electrical field. The

essence of field activation is to enhance densification of ceramic powders by decreasing the temperature and time of sintering, thereby considerably suppressing the grain growth. Field activated sintering technique (FAST) was applied to Al_2TiO_5 nanoceramics formed from BINARY Al_2O_3-TiO_2 powders obtained by sol-gel method. It was found that electric field activates formation of Al_2TiO_5 and its densification in the temperature range 1050-1250°C. The influence of electric field on Al_2TiO_5 formation, crystallization densification and final properties will be presented.

3:55 PM Break

4:05 PM Invited

Synthesis of Nanoparticles by a Novel Laser-Liquid-Solid Interaction Technique: *J. Singh*[1]; [1]Pennsylvania State University, Appl. Rsch. Lab., University Park, PA 16804 USA

A novel laser-liquid-solid interaction (LLSI) technique has been developed for synthesizing nanoparticles of materials including Ag, Ni, Ag-Ni alloy, SnO_2, Cu from liquid precursors. Rotating niobium substrates immersed in the liquid precursor were irradiated by a continuous wave CO_2 and Nd-YAG laser (λ = 1064 nm). Size and morphology of nanoparticles was dependent on various process parameters including laser energy, wavelength, precursor chemistry and interaction time. Two-phase alloys containing silver and nickel were fabricated by LLSI technique. The powders were characterized by x-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS) and high-resolution transmission electron microscopy (HRTEM). The synthesis mechanism of non-equilibrium Ag-Ni alloy nanoparticles has been proposed to occur primarily at the laser-liquid-solid interface by a nucleation and growth mechanism.

4:30 PM

Consolidation of Mechanically Alloyed Cu-In-Ga-Se Powders by a Field Activated Sintering Technique (Fast): C. Suryanarayana[1]; J. Curtis[2]; *J. R. Groza*[2]; [1]Colorado School of Mines, Dept. of Metallu. and Matls. Eng., Golden, CO 80401 USA; [2]University of California, Chem. Eng. and Matls. Sci., One Shields Ave., Davis, CA 95616 USA

Recently, copper indium diselenide ($CuInSe_2$)-based photovoltaic solar cells have received considerable attention due to a high conversion efficiency, up to 17.7% for a Cu-In-Ga-Se device. The present work presents an alternate processing route to the usually long deposition methods. The new approach involves mechanical milling of elemental powders followed by consolidation into bulk parts. Mechanical milling achieved powder blending and synthesis of the stoichiometric $CuIn_{0.7}Ga_{0.3}Se_2$ compound. The mechanically milled powders were consolidated to a 5.51 g/cm^3 density by a field assisted sintering technique. The final grain size was in the nanometer range (~ 63 nm, as determined by XRD Warren-Averbach method).

4:50 PM

A Unified Viscoplastic Model for Densification of Powder Compacts: *Hyoung Seop Kim*[1]; Yuri Estrin[2]; Elazar Gutmanas[3]; [1]Chungnam National University, Dept. of Metallu. Eng., Taejon 305-764 Korea; [2]The University of Western Australia, Dept. of Mech. and Matls. Eng., Nedlands, WA 6907 Australia; [3]Technion, Dept. of Matls. Eng., Haifa 32000 Israel

A model for densification of metallic powders is proposed. It involves viscoplastic constitutive equations based on dislocation density evolution and also accounts for effects of porosity. The model was applied to the case of cold powder compaction under uniaxial compression conditions. Densification behaviour during powder compaction was simulated using a combination of the implicit and explicit integration methods as applied to the dislocation density evolution and the variation of the relative density of the compact, respectively. The model was gauged by comparing the experimental data generated by the cylindrical die compaction tests on Cu powder with the simulation results.

5:10 PM

Synthesis of TiC/Fe-Al Nano-Nano Composites: *E. G. Baburaj*[1]; R. Fielding[1]; E. Nyberg[2]; F. H. (Sam) Froes[1]; [1]University of Idaho, Instit. for Matls. and Adv. Process., 321 Mines Bldg., Moscow, ID 83844-3026 USA; [2]Pacific Northwest National Laboratory, Battelle Blvd., P.O. Box 999, Richland, WA 99352 USA

This paper presents work on the formation of metal matrix composites formed from nanocrystalline TiC and Fe-Al. The nano-nano composite powder was produced by milling the commercially available pre-alloyed Fe-Al with ultrafine TiC powder. The high hardness and faceted nature of the TiC particles easily shears the Fe-Al powder particles to an ultrafine size, resulting in the formation of a nano-nano powder mixture. The reduction in particle size of Fe-Al as a function of milling time and TiC content has been investigated, using XRD and TEM. Consolidation of the powder mixtures to retain a nanoscale structure in the composites is in progress.

5:30 PM

Effect of Processing Parameters on Structure and Properties of Nanocrystalline FeCrP Electrodeposits: C. T. Kunioshi[1]; *L. V. Ramanathan*[1]; [1]Cidade Universitaria, Instit. de Pesquisas Engerget. e Nucl., C.P. 11049, São Paulo 05422-970 Brazil

Some nanocrystalline alloys have shown superior corrosion resistance and can be used to protect other materials less resistant in aggressive environments. Several techniques have been used to obtain nanocrystalline alloys and one of these is conventional electrodeposition. Fe-Cr-P alloy deposits were obtained from acid citrate baths using sodium hypophosphite as the source of P. The influence of processing parameters such as nature of complexing agent, bath current density, bath temperature and use of ion selective membranes on deposit characteristics such as crystallite size, composition, and morphology were investigated. The corrosion behavior of steel substrates coated with nanocrystalline Fe-Cr-P deposits under specific plating conditions was evaluated from potentiodynamic measurements in 0.05M sulphuric acid and 0.1M sodium chloride. Nanocrystalline deposits with ~6-7% Cr and average crystallite size of 15 A were obtained under a variety of plating conditions. Deposits obtained at ~100mAcm-2, in the presence of formic acid as complexant and after aging of the bath, were thick, homogeneous and adherent. The electrochemical tests revealed increased corrosion resistance of the nanocrystalline deposit covered surfaces, as compared to the uncoated surfaces.

5:50 PM

Electron Beam Modification of Nanostructured Materials: *Vadim J. Jabotinski*[1]; Francis H. (Sam) Froes[1]; [1]University of Idaho, Instit. for Matls. and Adv. Processes, Moscow, ID 83844-3026 USA

Electron beam processing offers great technical and economic capabilities of improvement of nanostructured materials. Heating combined with radiation treatment offering by the electron beam processing allows unique changes and modification in nanostructured materials. This paper will consider fundamentals and applications of the electron radiation in processing sintered powder components. The specific effects leading to increase in the component lifetime, wear, and heat resistance will be identified. Possible mechanisms for strengthening and improving the structure and creep performance will be discussed.