10TH INTERNATIONAL SYMPOSIUM ON EXPERIMENTAL METHODS FOR MICROGRAVITY SCIENCE: Session III

Sponsored by: ASM International: Materials Science Critical Technology Sector, Thermodynamics & Phase Equilibria Committee, Electronic, Magnetic & Photonic Materials Division/Structural Materials Division, Alloy Phase Committee, NASA Microgravity Sciences

Program Organizers: Robert Schiffman, R.S. Research Inc., Crystal Lake, Barton, VT 5822; Carlo Patuelli, Universita di Bologna, Depatrmento di Fisica, Bologna I-40126 Italy

Tuesday AM Room: Plaza Room A
February 17, 1998 Location: Convention Center

Session Chair: R. W. Smith, Queens University at Kingston, Department of Materials and Metallurgical Engineering, Kingston, Ontario K7L 3N6 Canada

8:30 AM

DIRECTIONAL SOLIDIFICATION OF TRANSPARENT ALLOYS WITH CONTINUOUS OBSERVATION OF THE 2D-GROWTH MORPHOLOGY IN TOP VIEW: T. Berrenberg[1]; T. Fuhrmeister[1]; B. Kauerauf[1]; *S. Rex*[1]; [1]ACCESS e.V., Aachen D-52072 Germany

During the recent spaceflight STS-84 a new facility for directional solidification of transparent alloys passed its maiden flight. This facility, called MOMO, mainly consists of a Bridgman type furnace for cylindrical samples in a glass ampoule and an endoscope optic to observe the growing solidification morphology in top view. The observation is imaged by a CCD camera and recorded on tape. The aim of related first experiment on MOMO was the investigation of the dynamic of cellular growth inside of a bulk sample. The paper will concentrate on the realized experimental set-up, its performance during the first application and on perspectives for future improvements.

8:50 AM

CHARACTERIZATION OF POLYMER DISPERSED LIQUID CRYSTALS PRODUCED IN MICROGRAVITY: *J. B. Whitehead, Jr.*[1]; M. M. Chandler[2]; L. J. Mathias[3]; [1]Department of Physics & Astronomy, [2]Department of Chemistry & Biochemistry, [3]Department of Polymer Science, University of Southern Mississippi, Hattiesburg, MS 39406

Polymer dispersed liquid crystal (PDLC) materials are produced in a microgravity environment to investigate the gravitational influence on the phase separated microstructure. PDLC materials contain micron-sized liquid crystal droplets dispersed in a solid polymer matrix. The phase separated microstructure determines the operating parameters (turn-on time, turn-off time, operating voltage, and contrast) of PDLCs. Therefore, a fundamental understanding of phase separation in this composite system is required to control the phase separated microstructure which will enable continued development of these materials to meet the demands of potential applications. Preparation of PDLC materials in a microgravity environment is advantageous for studying the aspects of phase separation which are masked in the terrestrial environment. PDLC materials were produced in the microgravity environment on board NASA's KC-135 aircraft using polymerization induced phase separation. The PDLC materials were characterized using scanning electron microscopy and laser light transmission.

9:10 AM

DIRECTIONAL SOLIDIFICATION OF MERCURY CADMIUM TELLURIDE IN MICROGRAVITY: Sandor L. Lehoczky[1]; *Donald C. Gillies*[1]; Frank R. Szofran[1]; Dale A. Watring[1]; [1]Marshall Space Flight Center, Huntsville, AL 35812

Mercury cadmium telluride (MCT) has been directionally solidified for ten days in the Advanced Automated Directional Solidification Furnaced(AADSF) on the second United States Microgravity Payload Mission (USMP-2). A second growth experiment is planned for the USMP-4 mission in November 1997. Results from USMP-2 demonstrated significant changes between microgravity and ground-based experiments, particularly in the compositional homogeneity. Changes were also observed during the microgravity mission which were dependent on the attitude of the space shuttle and the relative magnitudes of axial and transverse residual accelerations with respect to the growth axis of the crystal. Issues of shuttle operation, especially those concerned with safety and navigation, and the science needs of other payloads dictated the need for changes in attitude. One consequence for solidification of MCT in the USMP-4 mission is the desire for a shorter growth time to complete the experiment without subjecting the sample to shuttle maneuvers. By using a seeded technique and a pre-processed boule of MCT with an established diffusion layer quenched into the solid, equilibrium steady state growth can be established within 24 hours, rather than the three days needed in USMP-2. The growth of MCT in AADSF during the USMP-4 mission has been planned to take less than 72 hours with 48 hours of actual growth time. A review of the USMP-2 results will be presented, and the rationale for the USMP-4 explained. Pre-mission ground based tests for the USMP-4 mission will be presented, as will any available preliminary flight results from the mission.

9:30 AM

DENDRITE TIP MORPHOLOGY UNDER TERRESTRIAL AND MICROGRAVITY CONDITIONS: *J. C. LaCombe*[1]; M. B. Koss[1]; Afina Lupulescu[1]; L. T. Bushnell[1]; D. Corrigan[1]; M. E. Glicksman[1]; [1]Rensselaer Polytechnic Institute, Materials Science and Engineering Department, Troy, New York 12180-3590 USA

The development of dendritic patterns is dependent upon the transport of heat and solute near the advancing crystal-melt interface. The kinetics of this process were studied during recent space flights as part of the Isothermal Dendritic Growth Experiment (IDGE). Steady-state, dynamic tip shapes were observed under terrestrial and microgravity conditions, and analyzed using a quartic (4th-order) shape regression. This process yielded the parabolic tip radius, R, and tip speed, V, each of which are growth parameters already shown to be sensitive to the presence of gravitationally induced convection, whereas their combined sealing law, $VR^2=2\alpha d_0\sigma^*$, verified by these experiments, appears to be insensitive to the gravity level. Here α and d_o are the thermal diffusivity and capillary length, respectively, and σ^* is the scaling constant derived from theory. Additional analysis of these data shows that the three-dimensional dynamic tip shape also does not appear to be significantly affected by either the melt super cooling or the convective environment, providing additional evidence of a relationship between the scaling constant σ^*, and the shape of the dendrite tip.

9:50 AM

DIRECTIONAL SOLIDIFICATION OF IMMISCIBLE Al-In ALLOYS UNDER MICROGRAVITY CONDITIONS: *J. B. Andrews*[1]; L. J. Hayes[1]; Y. Arikawa[1]; S. R. Coriell[2]; [1]University of Alabama at Birmingham, Department of Materials and Mechanical Engineering, Birmingham, AL 35294; [2]National Institute of Standards and Technology, Gaithersburg, MD 20899

This presentation will cover the results obtained from three aluminum-indium samples which were directionally solidified aboard the Life and Microgravity Spacelab mission, STS-78. These samples were processed using an aluminum nitride ampoule assembly which contained several pistons and an elevated temperature spring. Directional solidification was carried out using the Advanced Gradient Heating Facility

(AGHF). Examination of the samples after the flight revealed the presence of voids of significant size in two of the flight samples with much smaller voids in a third. This presentation will discuss the source of these voids and the result of metallographic analysis of the directionally solidified samples.

10:10 AM Coffee Break in Exhibit Hall

10:30 AM
SOLID-LIQUID PRETRANSITIONAL PHENOMENA IN SHALLOW ENCLOSURES OF COMPOSITE PREFORMS: S. Coniglione[1]; *Carlo Patuelli*[1]; R. Tognato[1]; [1]Universita di Bologna, Dipartimento di Fisica, Bologna I-40127 Italy

Phase transitions often take place together with the so-called pretransitional phenomena which originates from the appearance of clusters of a competing phase inside a host phase. A composite material characterized by the presence of shallow enclosures together with a high number of catalytic positions has a high probability to present pretransitions phenomena. Infiltrated Al matrix composites reinforced with SiC whiskers or alumina fibers were heated below and above the liquidus temperature of the Al matrix and rapidly quenched. The crystallite size and the corresponding column lengths distributions were measured by X-ray diffraction line broadening Fourier analysis.

10:50 AM
COMPARATIVE DATA ON DIRECTIONALLY SOLIDIFIED Bi-Sn ALLOYS: R. Abbaschian[1]; *N. Barbosa*[1]; D. Allen[1]; T. Lenzi[1]; [1]University of Florida, Department of Materials Science and Engineering, Gainesville, FL 32611 USA

Dilute Bi-Sn samples were directionally solidified for 15 cm in a horizontal Bridgeman apparatus in order to generate the effect of gravitationally induced convection on the morphological instability of the alloy. The ground based experiments utilized the Seebeck thermoelectric effect to determine the solid/liquid interface temperature in the faceted alloys. Microstructural findings will be presented illustrating interfacial stability as a function of growth velocity and sample diameter. Morphological results will also be discussed and correlated with Seebeck results. The data is used as the terrestrial counterpart to the microgravity experiments in the USMP-4 shuttle flight, currently scheduled for November 1997.

11:10 AM
SELF ORGANIZING BEHAVIOR DURING EVAPORATIVE CRYSTAL GROWTH IN MICROGRAVITY: Lee Plansky[1]; Mike Mink[2]; *Keith Prisbrey*[2]; Penny Wikoff[3]; [1]INEEL, Idaho Falls, ID; [2]University of Idaho, Department of Metallurgical and Mining Engineering, Moscow, ID 33844-3024; [3]ERAD Inc., San Antonio, Texas

Convection-diffusion models can describe crystal growth and solid extension into the liquid interface. The process of crystal structure formation is arguably "self organizing", and can be compared to the "self organizing" behavior between nodes of neural networks during both supervised and unsupervised training. Microgravity removes buoyancy-driven convection in crystal growth process. The microgravity by evaporation of organic and inorganic salts in microgravity to earth-bound samples, and simulate the differences with neural networks. Procedures included examining both shuttle-grown and earth-grown structures with XRD, SEM, TMS, and other techniques, and modeling crystal growth with neutral networks. The result was a comparison of the influence of a "convective wave" of neural network weight training to convection in crystal growth. We concluded that the model has application to various coalescence, agglomeration, capillarity, Maragoni convection, and Ostwald ripening phenomena.

11:30 AM
BRIDGMAN SOLIDIFICATION OF CELLULAR ARRAYS IN A TRANSPARENT ORGANIC ALLOY: B. Kauerauf[1]; G. Zimmermann[1]; *S. Rex*[1]; [1]ACCESS e.V, Aachen D-52072 Germany

The investigation of the dynamic of cellular growth in directional solidification was the aim of a recent space-flight experiment on the STS-84 mission. In a Bridgman configuration a cylindrical sample of a Succinonitrile-Acetone alloy was repeatedly melted and solidified while the occurring cellular growth pattern was imaged in top-view by a CCD-camera. Of main interest were the onset of the planar - cellular transition, the evolution of first cells and the dynamic of the cellular pattern formations. The paper will present the results of this space experiment and outline first scientific findings on our knowledge about cellular growth.

11:50 AM
MUTUALLY SOLUBLE EFFECTS ON LIQUID PHASE SINTERED COBALT-COPPER SAMPLES: *James E. Smith, Jr.*[1]; Y. He[2]; A. K. Kuruvilla[2]; [1]University of Alabama, Dept of Chem & Matls Engrg, Huntsville, AL 35899 USA; [2]IIT Research Institute/MRF, Marshall Space Flight Center, Huntsville, AL 35899 USA

This paper documents the effect of composition and processing time on microstructural behaviors of Co-Cu samples that where liquid phase sintered under microgravity. Twelve (12) compressed powdered samples from Co-Cu system were processed during liquid phase sintering experiments aboard sounding rockets and on three Space Shuttle missions at different liquid fractions. Processing time ranged from 2.5 minutes to 66 minutes. Analysis of the microgravity sintered Co-Cu system shows that the samples exhibited pore formation and metamorphosis. A comparison between the Fe-Cu and Co-Cu systems is made in an effort to better understand the behavior of cobalt particles dispersed in this three-phase system. Microstructural characteristics such as densification, dihedral angle, contacts per grain, grain growth and pore metamorphosis extend our scientific understanding of mutally soluble alloy behaviors under liquid phase sintering conditions. Besides pore breakup, which was the major pore behavior in Fe-Cu samples, extensive pore filling and coalescence were observed in Co-Cu samples.

ADSORPTION, ION EXCHANGE, AND SOLVENT EXTRACTION: Ion Exchange I

Sponsored by: Extraction & Processing Division, Aqueous Processing Committee, Copper, Nickel, Cobalt Committee, Lead, Zinc, Tin Committee, Precious Metals Committee
Program Organizer: Courtney Young, Montana Tech, Metallurgical Engineering, Butte, MT 59701

Tuesday AM Room: Plaza Room C
February 17, 1998 Location: Convention Center

Session Chair: V. I. Lakshmanan, ORTECH Corp., Environmental & Materials Processing, Mississauga, ON L5K 1B3 Canada, Saskia Duyvestyn, University of Utah, Metallurgical Engineering, Dept of Met Engrg, Salt Lake City, UT 84112

8:30 AM INVITED
EX-SITU SURFACTANT CONDITIONING OF A FINELY-DIVIDED CHELATING RESIN TO IMPROVE FLOATABILITY: *Saskia Duyvesteyn*[1]; Dr. Fiona M. Doyle[2]; [1]University of Utah, Department of Metallurgical Engineering, Salt Lake City, UT 84112 USA; [2]University of California at Berkeley, Dept. of Materials Science and Mineral Engineering, Berkeley, CA 94720-1760 USA

Small ion-exchange resin beads provide faster mass transport than conventional-sized beads. Unfortunately, high pressures are needed to pump solutions through columns containing small resin beads. It is preferable to disperse fine resin in the solution being treated. Screens have been used to separate the resin from the solution, but screens do not retain fines created by attrition of the resin beads. We have developed a separation process based on flotation, which relies on the surface characteristics of the resin, instead of size. The resin is conditioned with a surfactant before dispersing it in the solution to be treated; this increases the hydrophobicity of the resin sufficiently for froth flotation, without introducing surfactant directly into the solution. The surfactant adsorbed on the resin surface does not appear to impair

the kinetics of metal ion removal. A flowsheet for an effluent treatment process is proposed; other applications are clearly possible.

8:55 AM INVITED

ADSORPTION AND DESORPTION OF SURFACTANTS ON A FINELY-DIVIDED CHELATING RESIN: *Saskia Duyvesteyn*[1]; Dr. Fiona M. Doyle[2]; [1]University of Utah, Department of Metallurgical Engineering, Salt Lake City, UT 84112 USA; [2]University of California at Berkeley, Dept. of Materials Science and Mineral Engineering, Berkeley, CA 94720-1760 USA

Small ion-exchange resin beads can be separated from solutions in which they have been dispersed by flotation. If the resin is conditioned with surfactant before contacting the pregnant/elution solution, it becomes sufficiently hydrophobic for effective flotation, without adding collectors to the solution being treated. To better understand the interaction of surfactants with a chelating resin, the adsorption and desorption isotherms of four different surfactants on Dow's XFS4195 resin were measured. The resin material used had a particle size of less than 125 γm. The four surfactants that were studied were: sodium dodecylsulfonate, sodium tetradecylsulfonate, sodium hexadecylsulfonate and dodecylbenzenesulfonic acid. The adsorption data could be described by a Langmuir adsorption isotherm. The monolayer concentration of the surfactants ranged from $1.5*10^{-3}$ to $2.2*10^{-3}$ moles per gram dried resin. Desorption was found to be reversible.

9:20 AM INVITED

SEPARATION OF Dy, Y, Tm AND Yb FROM HEAVIER RARE EARTH RESIDUE BY SOLVENT-IMPREGNATED RESIN: *Junji Shibata*[1]; Shigeno Matsumoto[1]; [1]Kansai University, Chemical Engineering, Osaka 564 Japan

Heavier rare earth metals which are in small amounts in minerals such as bastnaesite and monazite accumulate as residue due to the lack of suitable separation and purification methods. The heavier rare earth residue includes seven rare earth elements: Tb, Dy, Ho, Y, Er, Tm and Yb. Separation and recovery processes of Dy, Y, Tm and Yb from leached solution of the heavier rare earth residue were investigated using a column method with a solvent-impregnated resin. The solvent-impregnated resin was prepared by impregnating an organophosphorous extractant (PC-88A) into a macro-porous resin (Amberlite XAD-7). Previous attempts with simple adsorption/elution steps proved almost impossible to separate the four rare earth elements. However, this solvent-impregnated method proved viable by gradually changing eluent concentration from pH 2 to 2 mol/l HCl and using a development column. This separation process was proposed for recovering the rare earth metals from heavier rare earth residue.

9:45 AM INVITED

A NEW GENERATION OF COMMERCIAL ADSORBENTS: Xiangzhou Lin[1]; Graham Crooks[2]; Jim Dale[2]; *Bill Fries*[1]; [1]The Purolite Company, Bala Cynwyd, PA 19004; [2]Purolite International Ltd., Pontyclun, Wales CF72-8YL United Kingdom

Macronet adsorbents are composed of inner pore structures with a maximum of meso size pores. Internal surfaces are functionalized to enhance their compatibility with the treated medium in order to speed adsorption kinetics. Application examples include ethylene dichloride removal from waste water, hydromethylfurfural from high-fructose corn (HFC) syrups, and chloroform removal from a special effluent.

10:10 AM Coffee Break in Exhibit Hall

10:25 AM INVITED

POLYAMINE-SILICA COMPOSITES AS METAL RECOVERY MATERIALS: *David Pang*[1]; Susan Beatty[2]; Robert Fischer[2]; Edward Rosenberg[2]; [1]Purity Systems, Inc., Missoula, MT 59802; [2]The University of Montana, Department of Chemistry, Missoula, MT 59812

Although the binding of polymer systems to silica gels in the particle size range of 5-100um is well known, the full potential of these materials has yet to be realized. As metal sequestering media, these materials offer intrinsic advantages over resin-based materials including better thermal and mechanical stability as well as much faster capture kinetics. In order to compete with the established market, higher capacities and longer lifetimes under comparable conditions must be demonstrated. A collaberation between The University of Montana and Purity Systems Inc. has resulted in a recently patented class of polyamine-silica composites. The resulting material has a higher capacity and a longer lifetime than similar products such as a macrocycle-silica composite offered by another company. The results reported will include side-by-side comparisons with ion-exchange materials. Tests were conducted on a variety of industrial and mining waste streams including metal speciation tests on water from the Berkeley Pit (Butte, Montana) and ferrous waste streams from the Kelley Mine (Butte, Montana). Some recent results suggest that metal ion specificity may be related to polymer structure (i.e. branched backbone vs. linear-side chain). The relationship between polymer molecular weight and the silica-composites' metal ion capacity will also be discussed.

10:50 AM INVITED

USE OF ADSORPTION TECHNOLOGIES TO TREAT PROCESS EFFLUENTS - SELECTED CASE HISTORY: *V. I. Lakshmanan*[1]; [1]ORTECH Corporation, Environmental & Materials Processing, Mississauga, ON L5K 1B3 Canada

Absorption technologies have demonstrated themselves as viable process options to remove and/or recover metals and toxics from effluent streams processes in the mining and metallurgical industries. The paper will describe, with illustration, the removal of selected species eg: uranium, vanadium and cyanide.

11:15 AM INVITED

THE USE OF ION EXCHANGE RESINS AS SOLUTION TO TOXIC WASTE PROBLEMS: George L. Dimotsis[1]; *Frank X. McGarvey*[1]; [1]Sybron Chemicals, Inc., Birmingham, NJ 08011

Ion exchange resins are effective for the concentration of toxic waste produced by mining, metal plating, and other manufacturing industries. A full analysis of the water stream will establish the role to be played by ion exchange. Once the toxic elements have been concentrated, appropriate steps can be developed to dispose of the toxic substance economically. This paper covers the ion exchange processing of waste streams which contain lead, uranium, radium, mercury, arsenic, selenium, copper, chromium and zinc. Since each waste stream differs in composition, these elements will be considered individually from an ion exchange standpoint. Selection of the proper resins for particular applications will be discussed and the properties of commercially available resins received in a general fashion. Finally, ways to treat mixtures of metals and other non-toxic substances, problems related to resin stability, and economic situations based on disposal will be considered and discussed.

11:40 AM INVITED

MOLECULAR RECOGNITION TECHNOLOGY BASED REMOVAL OF IMPORTANT CONTAMINANTS FROM HYDROMETALLURGICAL STREAMS: *R. L. Bruening*[1]; F. P. Traczyk[1]; N. E. Izatt[1]; S. R. Izatt[1]; [1]IBC Advanced Technologies, Inc., American Fork, UT 84003

IBC Advanced Technologies, Inc. (American Fork, Utah, USA) has developed a number of highly specific ligands, based on molecular recognition technology (MRT), which are selective for impurities of importance to several hydrometallurgical industries. Impurities in the copper industry include bismuth, antimony, iron, chloride and cobalt. Bismuth and antimony can be extracted and recovered from a copper electrorefining tankhouse electrolyte, in pure form and with recycle of the eluents. Likewise, a variety of copper solvent extraction - electrowinning streams can be treated with MRT systems for extraction and recovery of iron, chloride and cobalt. Important impurities in the Zn industry include fluoride and chloride which can also be selectively removed using MRT. The development of these selective extraction materials and associated process systems allows for more efficient operation of present hydrometallurgical refineries. Engineering systems based on MRT are modular in design and have been implemented in the hydrometallurgical industries. Bench and pilot scale test results will be presented to demonstrate the high selectivity and efficiency of the technology as well as the economic feasibility of the process systems.

ALUMINA & BAUXITE: Workshop: Advanced Process Control

Sponsored by: Light Metals Division, Aluminum Committee
Program Organizer: Jean Doucet, Alcan International, PO Box 6090, Montreal, Quebec H3C 3A7 Canada

Tuesday AM Room: Fiesta A
February 17, 1998 Location: Convention Center

Session Chair: Jean-Pierre Riffaud, Alcan International Ltd., Montreal, Québec H3A 3G2 Canada

8:30 AM
PROCESS CONTROL IN ALUMINA REFINING - REVIEW AND PROSPECTS: *Dr. Jean-Pierre Riffaud*[1]; [1]Alcan International Limited, Montreal, Québec H3A 3G2 Canada

This paper will review the evolution of process control in the alumina industry. The comparison with others such as Oil and Gas will be useful to measure where we are now and what other steps, particularly in advanced control, we can envisage to bring value to our business. We will look at what this might (and will) imply both in terms of equipment infrastructure and development of the organization.

8:55 AM
OPPORTUNITIES FOR ADVANCED PROCESS CONTROL IN THE ALUMINA INDUSTRY: *Mr. Jim M. Langa*[1]; [1]Alcoa Laboratories, Alcoa Technical Center, Pittsburgh, Pennsylvania 15069 USA

In recent years, rapid changes in computing hardware and software technology have greatly increased the volume and accessibility of process information. The abundance of process information opens many opportunities to apply advanced techniques for process monitoring and control. Process information, which was once only "visible" in the control room, is now accessible worldwide, enabling development of plant wide (or even, worldwide) strategic business decision support systems. The alumina industry, like many other industries, is now beginning to exploit the potential of this technology. In this presentation, we will describe how advanced process control and information technologies are beginning applied to improve process monitoring and diagnostics, increase throughout and improve product quality, and to improve production planning and scheduling. The costs and benefits of these applications are discussed.

9:20 AM
NEURAL NETWORK MODELING FOR PROCESS ANALYSIS AND OPTIMIZATION: *Mr. Jay D. Coiclazier*[1]; [1]Fisher-Rosemount Systems, Austin, Texas 78754 USA

In the last several years, neural network modeling has been successfully used in numerous applications in the process industries. Most of these applications have focused on the development and implementation of virtual sensors. These virtual sensors can provide real-time predictions of key process or quality parameters. The financial benefits of these virtual sensor applications have been well documented. However, the benefits of neural network models extend beyond the development of virtual sensors. Neural network models can be a valuable tool for process analysis and optimization. This paper will discuss the use of neural network models for process analysis and optimization. The use of off-line post training sensitivity analysis will be demonstrated. This analysis can be used to identify and quantify the complex relationships between process measurements and key quality or performance values. The benefits of using neural network models to determine optimum operating conditions will also be discussed as well as some of the limitations and challenges. The paper will also highlight the importance of easy to use PC based software to perform the process analysis. Finally, the paper will discuss the use of on-line sensitivity analysis for process control and optimization.

9:45 AM
THE BENEFITS OF ADVANCED CONTROL FOR ALUMINA REFINING: *Dr. Neil Freeman*[1]; [1]Honeywell Hi-Spec Solutions Perth, Burswood, W.A. 6100 Australia

Advanced Control, and in particular Multivariable Predictive Control, have found widespread use within the petrochemical industry. Certainly within the last ten years, considerable use has been made of this technology from installations on Catalytic Cracking Units to Alkylation Units. Typical benefits from this control technology have been in excess of 2% improvement in profit. MPC (such as the Honeywell RMPCT) can be viewed as a tool to keep process variables at specified setpoints, just as a collection of single-loop controllers would do except that MPC will perform well with interacting variables where the collection of single-loop controllers would perform poorly. However, the real value of MPC is that it considers an entire process as a single entity rather than as a collection of isolated control loops. MPC then becomes a tool to keep the process within operational constraints while optimizing key performance measures. A typical alumina refinery has a large number of interacting processes: such as milling, digestion, washing, heat exchange, etc. These all incorporate considerable dead time which generally means that the processes are operated away from the true constraint because of the inadequacies of single-loop control. Enormous benefits can be gained through the application of multivariable predictive control, typcially in excess of several million dollars per year. This paper presents the basis for the application of advanced control to various processes within an alumina refinery together with the benefits to be derived.

10:10 AM Coffee Break in Exhibit Hall

10:25 AM
INFORMATION TECHNOLOGY AND PROCESS CONTROL FUTURE IN VAUDREUIL: *Mr. André Lalancette*[1]; [1]Alcan Smelters & Chemicals Limited, Vaudreuil Plant, Jonquière, Quebec G7S 4L2 Canada

The following presentation will contain essentially the five-year plan for Vaudreuil in terms of orientation, effort, challenges. It will also include the long term plan to optimize the infrastructures and available information put in place to attain the full business potential with improved control strategies, modified and improved administrative processes.

10:50 AM
WEB SERVER ACCESS TO PLANT DATA: *Mr. Bradley MacDonald*[1]; [1]Elsag Bailey (Canada) Inc., Process Industries Business Unit, Burlington, Ontario L7N 3N4 Canada

Traditional Process Control Systems have been installed as stand alone and autonomous systems with poor or limited connects to the office environment. Access to plant data for office users is often varied depending on the user. For example, engineers would use spreadsheet packages, financial people would use database (ODBC) connections and supervisors would use historical packages. The wide acceptance of the Internet and the Web Page (HTML) format has standardized the presentation of data within the workplace and greatly simplified how users view and access data. Web Servers can now be installed on company LANs to function as small private Intranet. These Web Servers can also be connected via firewalls to the Internet to offer Plant Data to the world. We would like to introduce the concept of a Process Information Web Server and explain how the Process Information Web Server could be the connection point between the process and the office users from the operator on the plant floor to the VP of Operation in the corporate office. Web Server Access will offer plant personnel a world of new opportunities.

11:15 AM Open Discussion

ALUMINUM REDUCTION TECHNOLOGY: Environmental

Sponsored by: Light Metals Division, Aluminum Committee
Program Organizer: Alton Tabereaux, Reynolds Metals Company, 3327 East Second Street, Muscle Shoals, AL 35661-1258

Tuesday AM Room: Fiesta D
February 17, 1998 Location: Convention Center

Session Chair: Margaret Hyland, University of Auckland, Auckland, New Zealand

8:30 AM

PERFLUROCARBON (PFC) GENERATION AT PRIMARY ALUMINUM SMELTERS: *Mr. Bud P. Leber, Jr.* [1]; Dr. Alton T. Tabereaux[2]; Dr. Jerry Marks[3]; Dr. Eric Jay Dolin[4]; Mr. Michael Gibbs[5]; Mr. Vikram Bakshi[5]; Dr. Brian Lamb[6]; Mr. Ravi Kantamaneni[7]; Mr. Touche Howard[7]; [1]Kaiser Aluminum, Spokane, WA 99218 USA; [2]Reynolds Metal Company, Muscle Shoals, AL 35661-1258 USA; Alcoa Technical Center, Alcoa Center, PA 15069-0001 USA; [4]U.S. EPA, Atmospheric Pollution Prevention Division, Wash., D.C. 20460 USA; [5]ICF-Kaiser Consulting, Universal City, CA 91601 USA; [5]ICF-Kaiser Consulting, Washington, D.C. 20006 USA; [6]Washington State University; [7]Indaco Air Quality Service, Inc; [7]Indaco Air Quality Service, Inc.

The primary aluminum industry is continually working to improve production efficiency and enhance environmental performance. As part of EPA's Voluntary Aluminum Industrial Partnership (VAIP) Program, twelve U.S. primary producers are focusing on reducing the duration and frequency of anode effects (AEs), which reduce aluminum current efficiency and generate two perfluorocarbons (PFCs), CF4 and C2F6. PFCs effectively trap heat in the atmosphere, contributing to the greenhouse effect. To better understand PFC emissions and key factors influencing their generation, VAIP sponsored a measurement program at seven aluminum smelters. The data show a clear trend toward lower PFC emissions with reduced AE duration. The scatter in the intra-plant and inter-plant data suggests there may be other operational factors affecting emission rates. The paper reviews the data, provides recommendations for improving PFC emissions predictability and suggests possible means for reducing these emissions.

8:55 AM

PFC EMISSION MEASUREMENTS FROM ALCOA ALUMINUM SMELTERS: *Dr. Jerry Y. Marks*[1]; [1]Alcoa, Alcoa VAIP Implementation Mgr., Alcoa Center, PA 15069 USA

Alcoa's Primary Metals USMS Operations has been a participant in the Voluntary Aluminum Industrial Partnership since the program's beginning. Excellent progress has been achieved in reducing anode effects from the 1990 baseline year defined by the program. Anode effect frequency has been reduced by 63% through 1996 against an overall target of 70% by the year 2000. An active PFC measurement program has also been carried out over this period to audit expected reductions of PFCs with reduced anode effects. Data is presented from measurements at five separate locations using three separate cell technologies. These data along with other data from the EPA sponsored measurements and data reported in the literature offer new insights into PFC emissions.

9:20 AM

THE EMISSION OF CARBONYL SULPHIDE FROM PREBAKE AND SØDERBERG ALUMINIUM CELLS: *Dr Knut Arne Paulsen*[1]; Dr. Jomar Thonstad[1]; Ms. Irene Utne[1]; [1]Hydro Aluminium Karmoy, Prosess Service Department, Karmøy N - 4265 Norway

The concentration of COS in the anode gas from prebake and Søderberg cells was studied by gas chromatography. Samples of undiluted anode gas showed that practically all the gaseous sulphur was present in the form of COS (~4000 ppm). Gas collected through a hole in the crust of prebake cells also showed fairly high concentrations of COS, whereas it was low under the gas collecting skirts of Søderberg cells, showing that COS was being oxidized to SO2 in the presence of air. The mass balanse with respect to sulphur in the raw materials and in the outlet gas (COS + SO2) was found to be fulfilled in prebake, and the rate of COS emission corresponded to 0.28 kg COS/tonne Al for prebake as well as Søderberg. A certain adsorption appeared to take place in the dry scrubber, while the subsequent wet scrubbing had little effect.

9:45 AM

FACTORS INFLUENCING HOODING EFFICIENCY: *Morten Karlsen*[1]; Nigel Anderson[1]; Nancy J. Holt[1]; Victoria Kielland[1]; Silja B. Vestre[1]; [1]Hydro Aluminium, Technology Center Ardal, N-5870 Ovre Ardal Norway

Different anode size and geometry have played an important role in the development of new and improved technology for reduction of aluminium since the invention of the Hall-Heroult process up. This has manifested itself by means of different anode superstructures, and thereby different ways of sealing off the process gases from the surroundings. In typical modern aluminium cells, anode size and hooding efficiency are important parameters of design for improved productivity and environmental results. Hooding efficiency is the result of a wide variety of construction parameters for the anode superstructure, where anode size and geometry are major contributors. To obtain an optimum design for new pot superstructures, it is important to study different pots with a wide variety of anode sizes and hooding methods. Potroom design and how these are ventilated, especially the airflow rising from the cellar through the gratings around the pot, are important parameters to obtain an overall excellent hooding efficiency during normal potroom operation. The design and operation of the system for evacuation of process gases (suction system) are other contributors for optimum hooding of the pots.

10:10 AM Coffee Break in Exhibit Hall

10:20 AM

SULFUR AND FLUORINE CONTAINING ANODE GASES PRODUCED DURING NORMAL ELECTROLYSIS AND APPROACHING AN ANODE EFFECT: *Mark M. R. Dorreen*[1]; Darrel Chin[1]; Jackie Lee[1]; Margaret M. Hyland[1]; Barry J. Welch[1]; [1]The University of Auckland, Dept. of Chemical & Materials Engineering, Auckland New Zealand

The anode gases evolved from a laboratory cell have been monitored to detect changes as an anode effect is approached. The cell was enclosed to prevent secondary reactions and the mass spectrometric method described elsewhere was used. Thermodynamic predictions have been made to ascertain the likely sulfur and fluorine containing species produced and these were compared to actual gases detected. Consistent with other recent articles, COS is evolved at a steady rate. Contrasting with potline duct analysis, no SO_2 could be detected. However, additional potroom studies have established that, when the crust is broken or the cell gas is burned, SO_2 is dominant. COF_2 has been detected in the period immediately before an anode effect. CF_4 production does not start until anode effect, where there is a relative increase in the amount of CO. A complementary thermodynamic analysis indicates that the formation of CF_4 and CO is associated with a chemical decomposition of COF_2.

10:45 AM

ESTIMATION OF FLUORIDE EMISSIONS FROM POTROOMS TO THE ATMOSPHERE: *Edgar Dernedde*[1]; [1]Kroll International, Jonquiere, Quebec G7S 3W9 Canada

The fluoride emission from a prebake pot can be evaluated from the Haupin model. The gas collection efficiency of a prebake pot can be determined from the gas exhaust rate, the hood open area and the heat loss from the alumina cover. The fluoride emission from an entire potroom to the atmosphere was estimated by a Monte Carlo simulation of the fluoride emission and the gas collection efficiency of all the pots in the potroom. Such simulations are useful for comparing different strategies (hood tightness, gas exhaust rate, operations) for minimizing the emissions to the atmosphere.

11:10 AM

NDIR MONITORING OF HYDROGEN FLUORIDE IN ALUMINIUM SMELTERS: IMPROVED LONG TERM STABILITY: *Dr. Pierre Bernard*[1]; Mr. Yvan-Martin Cyr[1]; Mr. Bruno Labranche[1]; Mr. Gilles Massicote[2]; Mr. Alain Morass[2]; Mr. Pierre Richard[2]; [1]National Optics Institute, Ste-Foy, Québec G1P 4N8 Canada; [2]Lauralco Inc., Deschambault, Québec G0A 1S0 Canada

Monitors specifically designed to measure hydrogen fluoride (HF) have been tested and evaluated over a period of 4 years. These instruments use a non-dispersive infrared spectroscopy (NDIR) technique. We have found that the limits of this, and probably most other techniques, have more to do with long term stability than short term sensitivity. Accordingly, the monitors were modified to incorporate a new automatic drift compensation technique that considerably improves the long term stability and overall performance. The monitors remain very robust with demonstrated low cost maintenance and ease of use. In particular, the light source is cheap and easily replaceable and the probe heads are chemically resistant. The use of fiber optic cables and a programmable microprocessor assures considerable flexibility: Results of tests and thorough in-situ calibration for monitors used in stacks and roof top vents of aluminum smelters (440 meters) will be given.

ATOMIC-LEVEL SIMULATION OF MATERIALS: NEW METHODS & NOVEL APPLICATIONS: Surfaces and Thin Films

Sponsored by: ASM International: Materials Science Critical Technology Sector, Computer Simulation Committee

Program Organizers: Jim Adams, Arizona State University, Dept. of Chemical Bio and Materials Dept., Tempe, AZ 85287-6006; Vaclav Vitek, University of Pennsylvania, Dept. of Materials Science & Eng., Philadelphia, PA 19104

Tuesday AM Room: 203
February 17, 1998 Location: Convention Center

Session Chair: Frederick Streitz, Auburn, AL 36849-5311

8:30 AM

MODELING COMPLEX CHEMICAL REACTIONS ON OXIDE SURFACES: *Dr. Kenneth C. Hass*[1]; Dr. William F. Schneider[2]; [1]Ford Motor Company, Physics Department, Dearborn, MI, 48121-2053 USA; [2]Ford Motor Company, Chemistry Department, Dearborn, MI 48121-2053 USA

General issues encountered in modeling the complex surface chemistry of oxides will be reviewed in the context of two specific reactions: the catalytic decomposition of NO by Cu-exchanged zeolites, and the dissociation of water on the basal plane of alpha alumina. Quantum chemical cluster calculations will be presented for both reactions, together with Car-Parrinello molecular dynamics (CPMD) simulations for the latter. Cluster methods are found to be especially useful for extracting qualitative understanding from detailed analyses of adsorbate binding and reaction pathways. Relatively simple cluster models for active Cu sites in zeolites reproduce many experimental observations and suggest a novel, kinetically-plausible, multi-step, catalytic cycle for NO decomposition based on short-lived, difficult-to-detect intermediates. Both cluster calculations and CPMD simulations for alpha-alumina indicate that H2O readily dissociates on an ideal Al-terminated basal surface. Although the two methods are largely complementary, the CPMD method provides qualitatively new insights because of its ability to treat higher water coverages and its explicit description of dynamical behavior. The following collaborators are gratefully acknowledged for their contributions to aspects of this work: J. B. Adams, W. Andreoni, A. Curioni, B. R. Goodman, W. L. Hase, H. B. Schlegel, R. Ramprasad, and J. Wittbrodt.

9:05 AM

MOLECULAR DYNAMICS STUDY OF ATOMIC CHLORINE SURFACE RECOMBINATION WITH COMPARISON TO EXPERIMENT: *David B. Graves*[1]; Bryan A. Helmer[1]; [1]University of California, Chemical Engineering, Berkeley, California 94720 USA

The recombination of chlorine atoms into chlorine molecules at surfaces is an important process in plasma reactors used for etching semiconductor materials in the microelectronics industry. In the case of silicon, atomic chlorine is considerably more reactive than molecular chlorine, and so the degree of dissociation in the plasma reactor has a strong influence on the etching rate. We have used molecular dynamics simulations of chlorine atoms adsorbing, diffusing, desorbing and reacting on chlorinated crystalline silicon surfaces in an attempt to understand the mechanisms of halogen atom surface recombination. The MD results were obtained at various surface temperatures and were combined with simple models of surface diffusion, thermal desorption and reaction to obtain a model expression for the temperature dependence of atomic recombination. The simulation and model results are in qualitative agreement with experimental measurements of recombination vs. surface temperature for crystalline silicon. The implications of these results for a wide class of radical-surface reactions in plasma processing is discussed.

9:40 AM

KINETIC MONTE CARLO SIMULATION OF DIAMOND CHEMICAL VAPOR DEPOSITION: *Prof. David J. Srolovitz*[1]; Mr. Corbett C. Battaile[1]; Dr. James E. Butler[1]; [1]University of Michigan, Materials Science & Eng., Ann Arbor, MI 48109-2136 USA

Kinetic Monte Carlo (kMC) simulations are used to analyze the growth of diamond from a hydrocarbon gas in a chemical vapor deposition (CVD) reactor. The only input to the present kMC simulations are the hydrocarbon reaction rates on the surface as a function of temperature and gas phase composition. The simulations are performed on a diamond cubic lattice. We will discuss the kMC algorithm and then present results on CVD diamond growth rates, morphology and defect incorporation. We will examine growth on both high symmetry and vicinal surfaces.

10:15 AM Coffee Break in Exhibit Hall

10:30 AM

AN ATOMISTIC SIMULATOR FOR DEPOSITION PROCESSES IN THREE DIMENSIONAL SPACES (ADEPT): *Dr. Hanchen Huang*[1]; Dr. Tomas Diaz de la Rubia[1]; Dr. George H Gilmer[2]; [1]Lawrence Livermore National Lab, Materials Sciences & Technology Division, Livermore, CA 94550 USA; [2]Bell Laboratories, Silicon Processing, Murray Hill, NJ 07974 USA

As miniaturization of semiconductor devices continues, filling trenches/vias becomes increasingly difficult. A robust simulator can help interpreting experimental results and guiding further experiments. A large effort has been devoted to developing robust simulators (e.g., SPEEDIE, SAMPLE, EVOLVE, DEPICT, SIMBAD, etc.). A lot have been learned using these simulators. However, as device size reaches deep submicron (0.25 to 0.10micron), width of the trenches/vias is on the order of hundreds of atomic layers. Atomistic processes dictate the deposition processes and must be treated at the corresponding level. Another important process, grain structure evolution, deserves better understanding in order to control film structure/texture. Using a hierarchy of simulation methods (ab initio, molecular dynamics, Monte Carlo) and experimental results, we develop an atomistic simulator. The molecular dynamics is employed to obtain information on atomic movement at fine time (pico- to nano-seconds) and space scale (nano meters). The ab initio and experimental results serve to calibrate the molecular dynamics results. A three dimensional lattice Monte Carlo model has been developed to study long time (up to hours) and large scale (microns) processes. A site in the lattice can be occupied by an atom from direct deposition or diffusion. A site on single crystal lattice is used to represent sites of all possible rotated lattices. A grain boundary is represented by high energy lattice sites, which are a result of carrying “mismatching bond”. Mass transport along grain boundaries is simulated by two processes: local reorientation and single atomic jump

facilitated by higher vacancy concentration, and their sum is matched with the molecular dynamics result. Microstructures, such as void and grain structure (nucleation, coarsening, and grain boundary grooving), of a thin film can be studied using this simulator.

11:05 AM

MICRON-SCALE KINETIC LATTICE MONTE CARLO SIMULATION OF THIN FILM GROWTH: Zhiyong Wang[1]; *James B. Adams*[2]; [1]Arizona State University, Science and Engineering of Materials Program, Tempe, AZ 85287-1704 USA; [2]Arizona State University, Department of Chemical, Bio, and Materials Engineering, Tempe, AZ 85287-6006 USA

A novel kinetic lattice Monte Carlo (KLMC) model has been developed and applied to the investigation of thin film growth. This model is capable of simulating growth of micron-scale systems by efficient memory usage and computational algorithms. This paper will describe how the model works and demonstrate its ability to simulate thin film growth processes, including deposition and diffusion.

11:25 AM

THE ROLES OF ATOMIC LEVEL SIMULATIONS IN DEPOSITION PROCESS SIMULATIONS: *Dr. Timothy S. Cale*[1]; [1]Arizona State University, Dept. of Chemical, Bio & Materials Eng., Tempe, AZ 85287-6006 USA

After summarizing the status of deposition process simulations that focus on the evolution of topography, the present and potential future roles for atomic level modeling and simulation in the evolution of deposited films will be discussed.

AUTOMOTIVE ALLOYS II: Session III - Applications

Sponsored by: Light Metals Division, Aluminum Committee
Program Organizer: Subodh Das, ARCO Aluminum Company, PO Box 32860, Louisvile, KY 40232

Tuesday AM Room: Fiesta B
February 17, 1998 Location: Convention Center

Session Chair: Subodh K. Das, ARCO Aluminum Company, PO Box 32870, Louisville, KY 40232

8:30 AM

INVESTIGATION OF CONTINUOUS CAST 5754Al AND 5754Al ALLOYS FOR POTENTIAL AUTOMOTIVE APPLICATIONS: *P. A. Friedman*[1]; A. M. Sherman[1]; [1]Ford Motor Company, Dearborn, MI 48121

Two continuously slab-cast aluminum alloys have been evaluated and compared with conventional ingot cast material for possible automotive body applications. The two alloys, 5754-O and 6111-T4, were compared in terms of mechanical properties, formability and microstructural attributes. Additionally, three different gauges of the 5754Al continuous cast sheet were tested in order to study the effects of sheet thickness on alloy properties. Microstructural analysis of these materials indicated slight differences between the continuous cast and respective ingot cast alloys in terms of grain structure and dispersoid density. Although the continuous cast alloys exhibited slightly different mechanical properties than their respective ingot cast alloys, preliminary formability testing indicated very little difference between these materials. Based on the results found in this study, it appears that these continuous cast alloys may become a viable alternative to conventionally-cast aluminum sheet for automotive body applications.

9:00 AM

STRENGTHENING IN THE NEW ALLOY AA6069: *S. C. Bergsma*[1]; M. E. Kassner[1]; [1]Oregon State University, Department of Mechanical Engineering, Corvallis, OR 97331; [1]Northwest Aluminum Company, The Dalles, OR 97058

AA6069, a new patented alloy has been developed for application in hot and cold extrusion and forging. The nominal composition is 0.85% Si, 0.25% Fe, 0.70% Cu, 1.35% Mg, 0.20% Cr, and 0.15% V. Average T6 properties of the ingot without hot or cold deformation are 415 MPa (60 ksi) ultimate tensile strength (UTS), 380 MPa (55 ksi) yield strength (4S) and 12% elongation. Average properties after hot and/or cold extrusion in the T6 condition range from 394 to 443 MPa (57 to 64 ksi) UTS, 353 to 387 MPa, (51 to 56 ksi) and 14 to 18% elongation. This alloy also has favorable fatigue and corrosion fatigue properties due to a combination of composition, high solidification rate, thermal and mechanical processing and T6 practice, careful TEM, SEM, optical metallography and EDS was used to characterize the precipitation features and the basis for improved mechanical properties over alloys such as 6061-T6. Current developmental applications include cold-impact air bag components, high pressure cylinders, and automotive wheels, suspension and drive train parts. The alloy is also much more scrap compatible than 2XXX and 7XXX alloys.

9:30 AM

ROLL FORMING TECHNOLOGY FOR MANUFACTURING AXISYMETRIC AUTOMOTIVE COMPONENTS: *C. K. Syn*[1]; D. R. Lesuer[1]; T. G. Nieh[1]; H. S. Yang[2]; K. R. Brown[2]; R. O. Kaibyshev[3]; E. N. Petrov[4]; [1]Lawrence Livermore National Laboratory, Livermore, CA 94551; [2]Kaiser Aluminum Center of Technology, Pleasanton, CA 94566; [3]Institute for Metals Superplasticity Problems, Ufa Russia; [4]Russian Federal Nuclear Center, Institute of Technical Physics, Snezhinsk Russia

A unique superplastic roll forming technology that permits complex axisymmetric components, such as automotive wheels and turbine disks, to be formed in a single forming operation, have been developed by two Russian institutes, the Institute of Technical Physics of Russian Federal Nuclear Center and the Institute for Metals Superplasticity Problems (IMSP). Current technology for making such components outside Russia requires either casting parts (with subsequent inferior mechanical properties) or forming several components followed by machining and welding operations. The superplastic roll-forming process offers the opportunity to manufacture a strong component in one continuous, economical operation. In addition, the process eliminates the need to manufacture the matched die sets that are required in conventional forging operations. Thus the cost of the dies and the time required to manufacture them can be eliminated. Automobile wheels were made by the process from a 6000 series aluminum alloy. Their microstructures and mechanical properties were evaluated at various locations of the wheels, preforms and blanks of the starting materials. The analyzed mechanical properties include the superplastic forming behavior at elevated temperatures. The roll-forming process and the results of microstructure and mechanical property evaluation will be presented.

10:00 AM

RECENT DEVELOPMENTS IN Al-MgMnSi-TYPE ALLOYS FOR AUTOMOTIVE APPLICATIONS: *Hubert Koch*[1]; Alois J. Franke[1]; [1]Aluminum Rheinfelden GmbH, Rhinfelden

The Al-MgMnSi alloys like Magsimal-59™ are being used increasingly for automotive applications because of their excellent properties in the as-cast condition. The preferred casting process is 1) high pressure diecasting with vacuum or forced venting systems or 2) squeeze-casting. Depending on casting application, a wide range of mechanical properties is possible. They include, for example high elongation (>14%) and medium yield strength or high yield (>200 MPa) and medium elongation. To meet these requirements under cost-efficient conditions, (i.e. no solution heat treatment at high temperatures and water quenching to avoid part distortion — a "low budget" heat treatment was developed for high-elongation requirements. Additionally, the influence of magnesium content has been studied to shift yield strength in the temper F (as-cast) condition. This paper describes and discusses results obtained through the use of scanning electron microscope (SEM)

analysis and metallographic studies. Castings developed for automotive applications are shown.

10:30 AM Coffee Break in Exhibit Hall

11:00 AM

WELDING PHENOMENA IN EXTRUDED ALUMINUM HOLLOW PROFILES: *Woiciech Z. Misiolek*[1]; Uday Chakkingal[2]; [1]Lehigh University, Institute for Metal Forming, Bethlehem, PA; [2]Monash University, Victoria Australia

A review of current research related to understanding of extrusion welding phenomena is presented. Two types of extrusion welds; the transverse and longitudinal welds are discussed. The metal flow and die design optimization is needed in order to minimize the amount of scrap metal as a result of transverse welding taking place during the billet-to-billet extrusion process. The importance of understanding of longitudinal weld performance and its metallurgical characteristics as a result of the extrusion process parameters is presented. Results of the preliminary tests for longitudinal weld obtained when a special test die was utilized are shown. An outline of proposed study involving laboratory simulation techniques to physically model the welding that occurs during extrusion of aluminum alloys through porthole dies is discussed. Mechanical properties of the welded samples need to be determined to investigate the influence of the extrusion parameters such as temperature, speed and die orifice location on weld quality. The relative performance of the welded region compared to adjacent regions need to be addressed as well. A necessity for mechanical evaluation of weld integrity both in the as-welded and in the aged condition is also discussed.

11:30 AM (ORAL ONLY)

SURFACE ROUGHENING AND STRAIN LOCALIZATION DURING FORMING OF MILL FINISHED AND MECHANICALLY SURFACE TEXTURED 6111 AND 6022 T4 ALUMINUM SHEETS FOR AUTOMOTIVE APPLICATIONS: G. W. Jarvis[1]; *H. R. Piehler*[2]; L. G. Hector[1]; R. Becker[1]; [1]Alcoa Technical Center, Alcoa Center, PA 15069; [2]Carnegie Mellon University, Department of Materials Science & Engineering, Pittsburgh, PA 15213-3890

Surface roughening during sheet deformation appears to be intimately linked to the strain localizations that typically precede the forming limits in both drawing and stretching. Surface roughening is further complicated when sheet surfaces are mechanically textured to entrap lubricant. Reported here are the results of large strain experiments on flat, mechanically textured 6111 T4 sheets deformed in the strain regime from pure shear to near plane strain. Four different surface textures (2 different crater depths for an hexagonal and a 45° screen pattern) were examined. Distributed lineal localizations were observed at angles consistent with those predicted for localized necking but at strain levels below those at which even diffuse necking would be expected to occur. The occurrence and angular positions of these distributed lineal localizations are also predicted from finite element simulations using the commercial code ABAQUS. Crater spacing appears to be more important than crater depth in initiating these instabilities. Preliminary experiments on 6022 T4 sheets are reported as well.

12:00 NOON

THE CAPABILITY AND METALLURGICAL ADVANTAGES OF AN INTEGRATED CONTINUOUS HEAT TREATMENT AND FINISHING LINE FOR THE PRODUCTION OF AUTOMOTIVE COIL AND SHEET: *G. J. Marshall* [1]; R. G. Hamerton[1]; A. R. Carr[1]; [1]Alcan International Limited, Oxon OX167SP England

The passenger vehicle of the future will be subject to the consumers desire sophisticated equipment that improves safety and comfort, as well as to environmental pressures to restrict fuel consumption. To meet these demands, car manufacturers are turning to the advantages of alternative materials and new design concepts that encourage lightweight vehicles and enhance fuel economy. To compete in this cost and quality demanding environment, aluminium producers will have to develop production facilities that match the varied needs of car manufacturers. The capability to produce aluminum strip in coil or sheet form with a variety of coatings, in sufficient quantity and of consistent quality is our challenge. Alcan has invested in a new facility in Nachterstedt, Germany commissioned in 1996, that will continue to supply the European automotive market well into the next century. Integrated into Alcan's European rolling system, the Nachterstedt plant is supplied from Alunorf (also in Germany) with economical, high quality hot and cold rolled coils. Subsequently, coils for the automotive industry are processed through the Nachterstedt continuous line designed to allow soft annealing or solution heat treatment (SHT), etching pre-treatment and coil coating options that meet the car industry's varied demands. The benefits of the new line are thus economic, technical, process and quality related. This paper will deal with the capability of the integrated line and the metallurgical advantages to the automotive sheet produced in this manner. In particular, the heat treatable 6xxx series alloys will be considered in terms of the SHT capability and the subsequent thermal exposures seen during surface finishing operations, such as paint curing. Furthermore, the technical benefits of utilizing pre-coated sheet will be discussed in terms of the formability enhancement in pressing operations.

12:30 PM

ELECTRODE DETERIORATION IN THE RESISTANCE SPOT WELDING OF ALUMINUM: Brent J. Frez[1]; Joanna R. Groza[1]; [1]University of California, Department of Chemical Engineering and Materials Science, Davis, CA 95616

Resistance spot welding (RSW) is a low cost, high productivity joining technique which is highly favored by the automotive industry. Questions were raised about the feasibility of RSW use in the welding of aluminum during the recent trend towards light vehicles. One of the main problems arising from RSW of aluminum is electrode life. It is our goal to understand the material science issues behind electrode deterioration. In order to accomplish this, we will perform welding tests in controlled conditions. The major parameters that will be varied are: electrode materials and microstructures, welding current level and wave form, applied pressure, and welding time. In order to asses electrode life, these tests will be run until failure. Different electrode geometries will also be investigated. SEM, X-ray diffraction, and optical microscopy techniques will be used for assessing the electrode deterioration and weld quality.

CARBON TECHNOLOGY: Retrofitting Anode Plants

Sponsored by: Light Metals Division, Aluminum Committee
Program Organizer: Ron Barclay, Alumax, PO Box 1000, Goose Creek, SC 29445

Tuesday AM Room: Fiesta E
February 17, 1998 Location: Convention Center

Session Chair: Juan Williams, Alumax Primary Aluminum Corporation, Goose Creek, SC 29445

8:30 AM

RECONSTRUCTION OF THE MIXING LINE FOR ANODE PASTE PRODUCTION AT ALUCAM: *C. Dreyer*[1]; C. Ndoumou[2]; J .L. Fadou[2]; [1]Aluminium Pechiney, 73300, St. Jean de Maurienne, Cedex France; [2]Alucam, Edea Cameroun

As part of a revamping program of the Alucam smelter, a Pechiney subsidiary in Cameroun, the mixing lines of the paste plant have been replaced by a new one. This 10 t/hour line fed with solid pitch, includes a Holoflite type oil preheater and two RV19 Eirich mixers, one for homogenization and the second one for cooling. Commissioned in March 1997 this line has rapidly brought a significant improvement of the anode quality. It represents a new step towards larger installation of the same design much less expensive than the conventional ones. A detailed description of the Alucam's installation is given with the pro-

cess parameters and the characteristics of anode now currently in this plant.

8:55 AM
INSTALLATION AND OPERATION OF A PITCH FUME COKE DRY SCRUBBER AT ALCOA MASSENA PLANT: *Bernard Cloutier*[1]; Douglas S. MacQueen[2]; [1]Procedair Industries, Montreal, Quebec Canada; [2]Alcoa, Massena Operations, Massena, NY USA

This paper will present the design parameters and scrubbing efficiency for a 30,000 ACFM pitch fume dry scrubber installed at ALCOA Massena. The system was started in December 1996 and is used as the standard for the other 5 ALCOA plants in the United States. Although pitch fume dry scrubbing is not new, this paper will focus on new requirements for these systems. More specifically coke fines are now injected at multiple locations in the upstream ductwork to prevent buildup and keep the ductwork clean (including the mixer vent pipes). The paper will also present the type of enclosure provided around the anode former for efficient capture of the fumes. This complete installation has not only allowed the Massena plant to comply with MACT standards but is providing much improved ambient air conditions for workers inside the carbon plant. ALCOA is also capable of reducing the building ventilation in the winter months which saves heating costs. The presentation will include: *A flow diagram of the installation including capture points, coke flow and main equipment sizing *Details of some specific hood design *Description of the in-duct coke fines injection system (8 injections points are included for the ductwork in Massena) *Details of venturi reactor and bag filter design *Scrubbing efficiency on POM's and particulate The coke fines used for pitch fume scrubbing are 100% reused for paste production.

9:20 AM
MODERNIZATION OF A PASTE PLANT: *R. Engelsman*[1]; H. van der Jagt[1]; A. Hordijk[1]; P. Sommer[2]; [1]Aluminium and Chemie Rotterdam B.V., 3197 KJ BOTLEK- Rotterdam The Netherlands; [2]Alesa Alusuisse Engineering, 8048 Zurich Switzerland

Most of the main machinery in the paste plant at Aluchemie had been in operation for thirty years. Major elements needed replacement. This paper describes the successful upgrading of the paste plant with only short production interruptions.

9:45 AM
KRASNOYARSK ALUMINUM ANODE PASTE PLANT: MODERNIZATION AND PHASE 1 CONVERSION TO DRY ANODE OPERATION: *Mr. John A. Johnson*[1]; Dr. S. V. Lobochev[2]; [1]Kaiser Aluminum Technical Services Inc., Pleasanton, CA 94566-7769 USA; [3]Krasnoyarsk Aluminum Smelter AO

In 1990 Kaiser Aluminum Technical Services Inc., at the Krasnoyarsk Aluminum Smelter AO, signed an agreement to modernize one line of the vertical stud Soderberg operation. In order to carry out this modernization, to support the production of dry anode paste, extensive modernization was required in the Anode Paste Plant. This presentation covers in detail the modernization of the Anode Paste Plant, the testing required to produce Kaiser dry anode technology with existing raw materials, the conversion to dry anode operation in Potroom 19 and the associated improvements in anode operation which resulted from the improvements made in the anode paste plant.

10:10 AM
NEW TOOLS FOR SUPERVISION AND CONTROL OF OPEN PIT ANODE FURNACES: *Dr. Wolfgang K. Leisenberg*[1]; [1]Innovatherm D-Butzbach/Polytec Giessen-Friedberg, D-61231

Since the quality of the anodes affects seriously the potline running cost, the baking process is, in terms of cost, one of the key sections in the aluminium production. So a defined and consistant quality is the task for a state-of-art heating and control system. In this field new methods have been developed in terms of diagnostic and control functions as are in key-words: Multivariable control, Area Interactions, Firing- and Baking Indexes, Fuel Efficiency Monitor, Flooding Monitor and Tele-Tuning. These more sophisticated methods will be explained and, in cooperation with the Gieβen-Friedberg Polytec and the operators of a new anode furnace control system, first results will be presented.

10:35 AM
REVAMPING OF ALBA ANODE PASTE PLANT (BARHEIN): A PROVEN EFFICIENT PROCESS FOR MIXING, PASTE COOLING AND PITCH VAPORS TREATMENT: *Mr. Jacques Lerouge*[1]; B. Hohl[2]; Jaffar G. Ameeri[3]; [1]FCB Mineral Processing and Carbon Plant Division, Cedex France; [2]EIRICH, 74736 Hardheim Deutschland; [3]Aluminium Bahrain, Manama Bahrain

In the middle of 1997, FCB has successfully commissioned the N° 1 anode paste plant. After more than 25 years operation, this plant has been entirely modernized and its production capacity increased. Anodes are produced from two existing hydraulic presses, which have been revamped too. The main purpose of this paper is to present the operation results of the solution adopted for mixing, paste cooling and pitch vapors treatment, based on the installation of one kneader and one mixer cooler feeding two hydraulic presses.

CAST SHOP TECHNOLOGY: Session IIA - Solidification Structures

Sponsored by: Light Metals Division, Aluminum Committee
Program Organizer: Diran Apelian, Worcester Polytechnic Inst., 100 Institute Rd., Worcester, MA 01609-2280

Tuesday AM — Room: River Room B
February 17, 1998 — Location: Convention Center

Session Chair: Angus Hellawell, Michigan Technological University, Houghton, MI

8:30 AM PLENARY PRESENTATION
MICROSTRUCTURE CONTROL IN INGOTS OF ALUMINUM ALLOYS WITH AN EMPHASIS ON GRAIN REFINEMENT: *D. A. Granger*[1]; [1]Grain Refining and Alloying Services, Murrysville, PA

9:10 AM
A COMPARISON OF THE BEHAVIOR OF AlTiB AND AlTiC GRAIN REFINERS : *W. Schneider*[1], M. A. Kearns[2]; M. McGarry[2]; A. J. Whitehead[3]; [1]VAW Aluminium AG, Bonn, Germany; [2]London & Scandinavian Metallurgical Co Limited U.K.; [3]Shieldalloy Metallurgical Corporation USA

AlTiC master alloys present a new alternative to AlTiB grain refiners which have enjoyed pre-eminence in cast houses for several decades. Recent investigations have shown that, under defined casting conditions, AlTiC is a more efficient grain refiner than AlTiB, is less prone to agglomeration and is more resistant to poisoning by Zr, Cr. Moreover it is observed that there are differences in the mechanism of grain refinement for the different alloys. This paper describes the influence of melt temperature and addition rate on the performance of both types of grain refiner in DC casting tests on different wrought alloys. Furthermore the effects of combined additions of the grain refiners and the recycling behavior of the treated alloys are presented. Results are compared with laboratory test data. Finally, mechanisms of grain refinement are discussed which are consistent with the observed differences in behavior with AlTiC and AlTiB.

9:30 AM
MODELLING OF THE EFFECTIVENESS OF Al-Ti-B REFINERS IN COMMERCIAL PURTIY ALUMINIUM: *A. M. Bunn*[1]; P. V. Evans[2]; D. J. Bristow[3]; A. L. Greer[3]; [1]University of Cambridge, Dept. of Materials science and Metallurgy, Cambridge CB2 3QZ U.K.; [2]Alcan International, Banbury, UK; [3]London & Scandinavian Metallurgical Co., Rotherham, UK

Al-5Ti-1B (wt.%) alloys are effective grain reginers for aluminium industry although as few as 1% of the TiB2 particles added to the melt nucleate grains. The aim of this work was to develop quantitative

modelling for prediction of grain sizes in commercial purity aluminium. In this way the low efficiency of refiners can be understood and the results of conventional grain-refining tests can be related to the grain sizes obtained in DC casting and other solidification processes. Ultimately the aim is to clarify the design rules for a more effective refiner. The modelling focused on the role of particle size and was supported by measurements of the particle size distributions in commercial Al-5Ti-1B refiners using scanning electron microscopy and image ana lysis. The effects on grain size of varying TiB2 particle size distribution, refiner addition levels, imposed heat extraction have been calculated. The model considers that nucleation of particles will be stopped by the onset of recalescence in the melt during solidification and that only those particles which are active growth centres at the point of recalescence will contribute towards the final grain size. Good agreement is found between the model predictions and conventional grain-refining tests.

9:50 AM

ON THE FADE OF GRAIN REFINEMENT OF ALUMINUM AND ALUMINUM ALLOYS BY THE AL-TI-B GRAIN REFINERS: *Tzu-Hsin Wang*[1]; Min-Hue Guo[2]; Shin-Li Chen[2]; Ching-Ling Liao[1]; [1]; [1]China Steel Corporation, Steel and Aluminum Research and Development Department and Deveo, Kaohsiung Tiawan ROC; [2]China Steel Aluminum Corporation, Hsiao, Kaohsiung Taiwan

The introduction of titanium and boron as inoculating agents of crystal nuclei for the grain refinement of aluminum and its alloys is a well developed casting practice. However, the grain refining effect fades away while holding the aluminum melt for a long period. The present work has investigated the variation of chemical composition of titanium and boron in the melt during holding time. It was found that the composition of these two elements decreased with the holding time and the resulting grain size in the casting was increased. On agitating the melt after prolonged holding time, the compositions of titanium and boron increased to the original values, along with the recovery of the grain refining effect. It indicates that the settling of inoculating elements and crystal nuclei is the primary reason and is responsible for the fading phenomenon of the grain refinement. The agitation brings the settled inoculating elements and crystal nuclei from the bottom melt back into the bulk melt and also recovers the grain refining effect of the melt.

10:10 AM

THE EFFECT OF GRAIN-REFINING ADDITIONS ON INTERMETALLIC SELECTION IN DILUTE ALUMINUM ALLOYS: *M. W. Meredith*[1]; A. L. Greer[1]; P. V. Evans[2]; [1]University of Cambridge, Department of Materials Science and Metallurgy, Cambridge CB2 3QZ UK; [2]Alcan International Ltd., Banbury Laboratory, Banbury OX16 7SP U.K.

The selection of second-phase intermetallic particles in the final stages of solidification of commercial-purity aluminum alloys depends on a number of parameters. This work concentrates on the effect of grain-refining additions. Steady-state solidification experiments were conducted to investigate flow grain-refiners indirectly influence the selection of intermetallics in the final microstructure. Solidification conditions were monitored and the solidification path compared with theory. The direct effect of grain-refiners on the nucleation of intermetallic phases was studied using the metallic glass technique. The glass-forming alloys used were based on compositions in the Al-Fe-M (M=Ce, La, Sm) system which crystallize directly to intermetallic phases. Nucleation on the grain-refining particles in the amorphous matrix can act as slow-motion analogue of processes in the melt and has the advantage of permitting microstructural study in the early stages of nucleation. Modelling of the nucleation and growth of intermetallics in Al-Fe has been attempted to explain the dependence of intermetallic selection on solidification conditions.

10:30 AM

THE GRAIN REFINING PERFORMANCE OF TICAR MASTER ALLOYS IN VARIOUS ALUMINUM ALLOY SYSTEMS: *A. Hardman[1];* D. Young[1]; K. B. Alloys, Inc., Robards KY

Abstract not available.

11:00 AM PANEL DISCUSSION WITH AUTHORS

DEFECTS IN CRYSTALS: A SYMPOSIUM HONORING THE CONTRIBUTIONS OF JOHN P. HIRTH: Crystal Plasticity

Sponsored by: Jt. Electronic, Magnetic & Photonic Materials Division/ Structural Materials Division, Chemistry & Physics of Materials Committee

Program Organizers: Craig S. Hartley, National Science Foundation, 4201 Wilson Blvd Room 545, Arlington, VA; Brent L. Adams, Carnegie Mellon University, Dept. of Materials Sci & Eng., Pittsburgh, PA 15213-3890; Richard G. Hoagland, Washington State University, Dept. of Materials Sci & Eng., Pullman, WA 99164-2920; Rob Wagoner, The Ohio State University, Dept. of Materials Sci & Eng., Columbus, OH 43210

Tuesday AM Room: 102
February 17, 1998 Location: Convention Center

Session Chair: Prof. William D. Nix, Stanford University, Dept. of Matls. Sci & Engr., Stanford, CA 94305-2205 USA

8:30 AM

IMPLICATIONS OF DISLOCATION MICROMECHANISMS ON CHANGES IN ORIENTATION AND SHAPE OF SINGLE CRYSTAL SUPERALLOYS: *M. Ardakani*[1]; B. A. Shollock[1]; Professor Malcolm McLean[1]; [1]Imperial College of Science, Technology and Medicine, Department of Materials, London SW7 2BP UK

An understanding of the mechanisms controlling the anisotropic deformation of single crystal superalloys is a prerequisite for establishing reliable constitutive laws for engineering design. It is clear that, in view of the variation in the level of creep anisotropy with temperature and stress that is observed experimentally, the anisotropy in creep strength cannot be explained in terms of Schmid law concepts and the operation of a single slip system. However, there remains some debate over the details of the dislocation systems that do contribute significantly to the high temperature deformation. There have been reports and proposals that creep predominantly occurs by viscous glide of various combinations of dislocations with Burgers vectors of types, and the authors have recently observed profuse mechanical twinning in both SRR99 and CMSX4 under relatively low temperature/high stress conditions. However, it is difficult to identify positively the operating slip systems by (a) conventional X-ray techniques because of deterioration in resolution of the diffraction images with increasing plastic strain and (b) anisotropy of mechanical properties because of ambiguities in their interpretation. This paper will consider the consequences of the different possible slip and twinning systems on changes in crystal orientation and of specimen shape that should occur during creep deformation during tensile loading in various complex crystallographic directions. These predictions will be compared with experimental measurements of crystal rotations (using electron backscatter diffraction) and of the change in cross-sectional shape (initially circular) that occur as a consequence of creep strain. It is quite clear that in conditions when the resolved shear stress for deformation is low, such as for tensile stresses oriented close to<lll> and<110>, one of the other deformation modes is dominant. The possibility of simultaneous operation of two or more slip systems leads to a range of possible crystal rotation trajectories and shape changes. The influence of various microstructural features, such as g' morphology/distribution and casting porosity, in modifying the purely crystallographic analysis of deformation characteristics will be considered. An anisotropic model of creep deformation, encompassing these micromechanical concepts, has been developed

and its ability to represent a wide range of types of mechanical behavior will be described.

9:00 AM

ANISOTROPIC ELASTICITY STUDIES OF WORK HARDENING IN EPILAYERS: *Professor Tong-Yi Zhang*[1]; [1]Hong Kong University of Science and Technology, Department of Mechanical Engineering, Kowloon, Hong Kong PRC

Anisotropic elasticity approach is used to study mismatch dislocations in the interface between an epilayer and its substrate. The results show that sequential generation of a dislocation requires an additional work component due to the interaction between the fresh dislocation and pre-existing dislocations, which causes work hardening. When the distance between the fresh dislocation and the nearest pre-existing dislocation is comparable to the layer thickness, the additional work component achieves the level of the self energy of an isolated dislocation. The additional work increases sharply with decreasing distance between the fresh and pre-existing dislocations. If the distance exceeds approximately twenty times the layer thickness, the additional work becomes insignificant. These results are consistent with experimental observations.

9:20 AM

IN SITU MEASUREMENTS OF DISLOCATION STRUCTURE EVOLUTION: *Dr. L. E. Levine*[1]; Dr. G. G. Long[1]; Dr. D. R. Black[1]; Dr. Robb Thomson[1]; [1]NIST, Ceramics Div., Gaithersburg, MD 20850

The evolution of dislocation structures in plastically deformed metals are directly responsible for the observed changes in mechanical properties. In spite of the importance of this effect, numerous technical difficulties made in situ measurements of this process impossible until very recently. We present experimental results from both ultra-small-angle X-ray scattering (USAXS) and high-resolution diffraction imaging on single-crystal Al samples deformed in situ on beam line X23A3 at the National Synchrotron Light Source. Data were obtained at strains from 0% to 12% strain. Stress-strain data were obtained simultaneously with the X-ray data. A new theory for X-ray scattering from dislocation structures allows quantitative interpretation of the USAXS data.

9:40 AM

CHARACTERIZATION AND CONTROL OF CHAOTIC STRESS OSCILLATIONS IN A MODEL FOR THE PORTEVIN-LE CHATELIER EFFECT: *Alan J. Markworth*[1]; A. Gupta[1]; R. W. Rollins[1]; [1]The Ohio State University, Department of Materials Science and Engineering, Columbus, OH 43210 USA

Dynamical properties of a four-dimensional model of the Portevin-Le Chdtelier effect (Solid State Phenomena 42-43, 277 (1995).) are considered. The model describes a specimen being plastically deformed at constant strain rate. A plastic instability, resulting from coupled interactions between the system variables, i.e., three different dislocation densities and the specimen stress, causes the stress to undergo chaotic oscillations within certain ranges of the system parameters. The chaotic behavior is quantified in terms of its Lyapunov exponents, and the Lyapunov dimension of the chaotic behavior is found to be about 2.2 for the parameter values that are used. It is shown that the oscillations can be completely suppressed using a simple and physically realistic feedback-control strategy. This research is supported by the Electric Power Research Institute, Palo Alto, Calif., under Contract WO9000-35.

10:00 AM

STRENGTHENING OF LOW-INTERSTITIAL STEELS BY STRAIN-AGEING TREATMENTS: *James N.A. Starling*[1]; S. Saimoto[1]; J. D. Boyd[1]; [1]Queen's University, Department of Materials and Metallurgical Engineering, Kingston, Ontario K7L 3N6 Canada

Formable "interstitial free" (IF) automotive sheet steels can be designed to achieve a 30-50 MPa strength increment during paint baking. The strengthening mechanism is a combination of C segregation to dislocations and precipitation of coherent Fe carbides. The bake hardening (BH) is controlled by the amount of solute C available following the industrial rolling - annealing - forming process. This paper describes the effects of the annealing process variables (temperature, time, cooling rate) on BH for a series of IF steels having Nb/C ratios of 0.7 - 1.5. Solute carbon concentrations are determined by i) measurement of the ageing index, ii) calculation from changes in NbC volume fraction, and iii) measurement of activation volume by strain rate change experiments. The solute C concentration is correlated with BH using strain ageing models.

10:20 AM

EXPERIMENTAL STUDY OF THE STABILITY OF DISLOCATION STRUCTURES IN COPPER POLYCRYSTALS PRODUCED THROUGH CYCLIC DEFORMATION: *Zhirui Wang*[1]; [1]University of Toronto, Department of Metallurgy and Materials Science, Toronto, Ontario 5S 3E4 Canada

The stability of dislocation structures in OFHD Cu polycrystals formed during cyclic deformation was studied experimentally. The experimental procedure involved several steps: First, cyclic deformation was performed so as to let the material accommodate a certain amount of plastic strain; second, the deformed samples were cut and annealed at different temperatures; third, TEM (Transmission Electron Microscope) observation was carried out using thin films prepared with samples annealed at various temperatures to investigate the changes of the dislocation structures; and finally, DSC (Differential Scanning Calorimeter) tests with the deformed samples were carried out to monitor the process of thermal activities during annealing. For a comparison, samples of same material were deformed in the way of cold rolling and were then also tested with the same procedure used for cyclic deformation samples. Results show that the cyclically formed dislocation structures sire much more stable than that formed in static deformation. Typical evidences are: The change of cyclic deformation induced structures was found to be very gradual. The wall structures rurmed in cyclic deformation kept its structure profile until over 500ºC, whereas the debris formed in static deformation disappeared at much lower temperature. No apparent heat release peak was detected in the DSC testing with the fatigued samples, but a clear peak was observed with the statically deformed sample. Detailed results and their discussions will be all presented.

10:40 AM

THE STUDY OF DISTORTIONS AND DEFECTS IN NANOMETALLIC CLUSTERS: *Professor Miguel Jose Yacaman*[1]; Dr. C. Zorrilla[1]; Dr. S. Tehuacanero[1]; Dr. M. Espinosa-Pesqueira[1]; Dr. J. A. Ascencio[1]; [1]Universidad Nacional Autonoma de Mexico, Instituto de Fisica, Mexico, D.F. 01000 Mexico

Clusters and particles in the nanometer size are very important in many modern applications of materials. An understanding of their structure is important for designing materials with new properties. A systematic study of crystal structure and lattice distortions metal particles was performed using a number of experimental techniques (TEM, EELS, EDS, Pixe and X-Ray Diffraction) and theoretical calculations. In particular we have measured the interplanar distance on gold particles of 10-15 Angstroms. We measured distances atom by atom using a High Resolution Image matched with computer calculations. We conclude that the particles show irregular distortions up to a value of 10% with respect to the bulk value. This technique allows to map in a two-dimensional fashion the distortions on the particles. The results are discussed in terms of the minimization of the total energy of the particle. We also pointed out the effect of such distortions on the optical properties of those nanoparticles.

11:00 AM INVITED

MESOSCALE INVESTIGATIONS OF THE DEFORMATION FIELD IN CRYSTALLINE MATERIALS: *Brent L. Adams*[1]; [1]Carnegie Mellon University, Department of Materials Science and Engineering, Pittsburgh, PA 15213-3890 U.S.A.

It has recently been demonstrated that orientation imaging microscopy can be adapted to study the fields of lattice curvature in deformed crystalline materials. From curvature measurements it is convenient to obtain lower-bound estimates on the distribution of geometrically-necessary dislocation (GND) densities. Applications to the study of deformation near the interfaces of high purity aluminum bicrystals are described. Comparisons of the experimental results with finite-element simulations of the deformation field, obtained using finite elastic/crys-

tal-plastic constitutive laws, are presented. The results show a varied interaction of grain boundaries with the deformation field. At (maximum principal) strain levels larger than 0.2 the interfaces studied exhibited a sink-like behavior (reductions of some components of the GND density near the interface) which was not predicted by simulation.

GENERAL ABSTRACTS: IV - Deformation

Sponsored by: TMS

Tuesday AM Room: Patio A
February 17, 1998 Location: Convention Center

Session Chair: John Vetrano, Pacific Northwest National Laboratory, Richmond, Washington 99352

8:30 AM
DISLOCATION CLIMB IN NiAl SINGLE CRYSTALS: *Xiaoli Shi*[1]; S. Mahajan[1]; T. M. Pollock[1]; V. S. Arunachalam[1]; [1]Carnegie Mellon University, Dept. of Materials Science and Engineering, Pittsburgh, PA 15213

To gain a better understanding of dislocation climb in intermetallics, we have investigated the annealing kinetics of prismatic loops in NiAl single crystals. To produce these loops, the samples oriented for single slip were deformed at ambient temperature. The deformed samples were annealed at 673K for 5 hours to break up the deformation-induced dipoles into loops. These base-line specimens were then annealed for different times at different temperatures to measure the annealing kinetics, and to determine the activiation energy associated with climb. These results will be presented and discussed in the light of our modeling work on dislocation climb. The above work was supported by Dr. G. Yoder of ONR and the authors gratefully acknowledge the support.

8:50 AM
THE BAUSCHINGER EFFECT IN POLYCRYSTALS OF Ni3Al WITH AND WITHOUT BORON: *E. M. Schulson*[1]; Y. Xu[1]; [1]Dartmouth College, Thayer School of Engineering, Hanover, NH 03755

Experiments have revealed that polycrystals of the Ni-based intermetallic Ni3Al exhibit the Bauschinger effect and that boron lessens its magnitude by about 70%. The attendant back stress is attributed to internal stresses generated by the piling up of dislocations at grain boundaries. The boron-induced reduction is attributed to the enhancement of slip transmission across grain boundaries. The results will be discussed in terms of the boron-induced brittle-to-ductile transition.

9:10 AM
EFFECT OF STABILITY ON THE AMBIENT TEMPERATURE CREEP DEFORMATION OF BETA TITANIUM ALLOYS*: *Anand Ramesh*[1]; Sreeramamurthy Ankem[1], [1]University of Maryland, Department of Materials and Nuclear Engineering, College Park, MD 20742

It has been shown that ambient temperature creep strain of a β Ti-13%Mn alloy at 95% yield stress is negligible. The system currently under investigation is a β Ti-14.8%V alloy. The creep strain of this alloy was found to be significantly higher than that of a β Ti-13%Mn alloy. Further, additional deformation mode(s) were found in the Ti-14.8%V alloy. This suggests the possibility that ambient temperature creep strain and deformation modes depend on the stability of the β phase. Details of the investigation will be presented. *This work is being supported by the Office of Naval Research under grant number N0001996101819.

9:30 AM
SYNCHROTRON X-RAY OF DISLOCATIONS IN ICE: *Dr. Ian Baker*[1]; X. Hu[1]; D. Cullen[1]; X. Li[1]; M. Dudley[1]; D. Black[1]; [1]Dartmouth College, Thayer School of Engineering, Hanover, NH 03755

Over the last few years Synchrotron x-ray topography has been used to study the deformation of both polycrystalline and single crystal ice. In this presentation, the behavior of dislocations around loaded notches in single crystal ice will be presented in terms of both the orientation of the crystal and the temperature of deformation. The effect of impurities on the behavior of dislocations in single crystal ice will also be presented. This work was supported by the Army Research Office through grant no. DAAH04-96-1-0041 and the National Science Foundation through grant no. DPP-92-18366.

9:50 AM
MECHANICAL ANISOTROPY AND FORMABILITY OF TEXTURED ZIRCALOY SHEET: *Susan A. Lloyd*[1]; K. Linga Murty[1]; [1]North Carolina State University, Raleigh, NC 27695

Zirconium alloys which are commonly used in light water reactors, exhibit preferred orientations or textures due to their hcp crystal structure and limited number of slip systems. Resulting anisotropic mechanical properties in turn affect their formability, which has technological significance in the productivity of the components. We report here a study on the mechanical anisotropy of Zircaloy sheet fabricated from two different routes, one sheet having good formability, and the other not good formability. Square grids were electro-chemically etched on one side of tensile specimens, and changes in grid size along the longitudinal and transverse directions were determined. These changes in grid size along the two directions were measured following plastic de formation. Thus, the contractile strain ratios, R and P, which are also the mechanical anisotropy parameters in Hill's formulation for generalized stress, were evaluated. Backofen formability parameter (β) is related to R and P, and the β-values determined on the sheets revealed high values for the good material. Work is in progress on the texture evaluation and plasticity modeling to predict the mechanical anisotropy and formability of these materials, and progress to-date will be presented. This work has been supported by the National Science Foundation Grant #DMR-9504818.

10:10 AM Coffee Break in Exhibit Hall

10:20 AM
INFLUENCE OF TEXTURE AND INTERSTITIAL CONTENT ON THE STRUCTURE/PROPERTY RESPONSE OF ZIRCONIUM: *Dr. G. C. Kaschner*[1]; Dr. G. T. Gray, III[1]; Dr. S. R. Chen[1]; [1]Los Alamos National Laboratory, MST-5, Los Alamos, NM 87545 USA

The effects of texture and interstitial impurities on deformation twinning in zirconium (Zr), in addition to variations in strain rate and temperature, are utilized to probe substructure evolution and mechanical behavior. The compressive yield response of strongly textured high-purity crystal-bar and commercial purity Zr was found to depend on the loading orientation relative to the h.c.p. c-axis, the applied strain rate, varied between 0.001 and 5000/s, and the test temperature, varied between 76 and 823K. The rate of strain hardening in Zr was seen to depend on the controlling defect storage mechanism as a function of texture, strain rate, and temperature.

10:40 AM
INFLUENCE OF AN ELECTRIC FIELD ON THE SUPERPLASTIC DEFORMATION OF Zn-10[1]: *Dr. Hans Conrad*[1]; Dr. Di Yang[1]; [1]North Carolina State University, Materials Science & Engr. Dept., Raleigh, NC 27695-7907 USA

The effect of a dc electric field of 1 kV/cm on the superplastic deformation of the Zn-10A1 alloy at 280°C was investigated at initial strain rates in the range 6.7×10^{-4} - 67×10^{-4} s^{-1}. The field increased the flow stress and decreased the amount of cavitation, the magnitude of which decreased with strain rate. The value of the stress exponent $n = d\ln\varepsilon/d\ln\sigma$ was ~2, and was relatively independent of the electric field. When the electric field was turned "on" and "off" during the course of a test at 6.7×10^{-4} s^{-1}, there occurred an increase in strain hardening rate when the field was turned "on" and a decrease when it was turned "off". The mechanism(s) by which the field affects the plastic flow and cavitation are considered.

11:00 AM

EFFECT OF AN ELECTRIC FIELD ON THE PLASTIC DEFORMATION AND FRACTURE OF POLYCRYSTALLINE NACLTHE INFLUENCE: *Dr. Hans Conrad*[1]; Dr. Di Yang[1]; [1]North Carolina State University, Department of Materials Science and Engineering, Raleigh, North Carolina 27695-7907 USA

The influence of an electric field E<0.1 MV/m on the plastic flow and fracture of cast polycrystalline NaCl was determined in compression at room temperature. Without an electric field the major slip system was deduced to be {110} <110>, with impurity-cation-vacancy dipoles being the short-range obstacles to dislocation motion. The initial strain hardening rate was similar in magnitude to that for Stage II in single crystals; its decrease with strain was attributed to cross slip. Plastic flow preceded fracture, which was intergranular without an electric field. The yield, flow and fracture stresses and the strain hardening coefficient decreased with electric field, an approximately 50% decrease occurring at E = 0.1 MV/m. This field is one-to-two orders of magnitude lower than had previously been found to produce significant effects in NaCl single crystals. The fracture mode with the field was mixed cleavage and intergranular. It is concluded that the major effect of the electric field was to enhance cross slip, thereby reducing the rate of strain hardening and in turn the flow and fracture stresses.

11:20 AM

THE EFFECT OF PLASTIC STRAIN ON THE ELASTIC BEHAVIOR OF SHEET METALS: *Ms. Ruth M. Cleveland*[1]; Professor Amit K. Ghosh[1]; [1]The University of Michigan, Department of Materials Science and Engineering, Ann Arbor, MI 48109-2136 USA

Elastic loading and unloading behavior of sheet alloys of 6022 Al and high strength steel have been studied at different levels of uniaxial plastic pre-strain. Loading and unloading were performed at a constant strain rate of 5 x 10-4 s-1. A difference was recorded between loading and unloading moduli for both materials, and the average elastic modulus was found to decrease with increasing pre-strain for both loading and unloading stages. Elastic region also became more non-linear with increasing plastic strain. This effect was significantly more pronounced for the high strength steel, which exhibited more non-linearity at all pre-strain levels. The experimentally observed shape of the unloading curves has been modeled with a 2nd order polynomial equation and an experimental relation between pre-strain and modulus determined for each alloy. The non-linearity and the modulus decay have been analyzed in terms of internal stress and rate dependent deformation.

11:40 AM

HIGH STRAIN RATE BEHAVIOR OF BERYLLIUM: *Dr. William R. Blumenthal*[1]; Mr. Stephen P. Abeln[1]; Mr. Douglas D. Cannon[1]; Dr. George T. Gray, III[1]; [1]Los Alamos National Lab., MST-5, Los Alamos, NM 87545 USA

The compressive stress-strain response of three commercial grades of beryllium were studied as a function of strain rate and temperature. Brush Wellman grades S200D, E, and F represent a historical perspective of beryllium processing from the 1960's through 1990's. The purpose of this study was to measure the mechanical behavior of these grades of beryllium over a wide range of deformation conditions and to correlate this behavior with microstructural evidence for deformation mechanisms. The compressive stress-strain response was found to be strongly dependent on the applied strain rate between 0.001 and 8000 s-1 and on the temperature between 77°K and 873°K, but was virtually independent of grade. Microstructural examination of split Hopkinson pressure bar specimens revealed that twinning was extensive at strains above 7% and that samples deformed to 20% strain contained both twinning and grain boundary microcracking.

GENERAL ABSTRACTS: VII - Materials Processing I

Sponsored by: TMS

Tuesday AM Room: Patio B
February 17, 1998 Location: Convention Center

Session Chair: Keith Axler, Los Alamos National Laboratory, Nuclear Matls. Div. MS E506, Los Alamos, New Mexico 87545-454

8:50 AM

EXTENSION OF ALUMINUM MELTING & HOLDING FURNACE LIFE USING CERAMIC WELDING: *Stephen D. Cherico*[1]; [1]FOSBEL, INC., Berea, OH 44017

For over fifteen years, the lives of furnaces of all types have been extended by the use of a refractory repair technology known as "Ceramic Welding". After years of development and testing, this versatile technology is proving to be a viable, cost-effective means of repairing and maintaining aluminum melting and holding furnaces. The patented process uses a specially developed mixture of refractory and metal powders which, when applied, undergo an exothermic reaction, depositing a fused refractory material onto the damaged or degraded area, restoring it to its original integrity. While originally developed for belly band erosion, the process has also been shown effective in a variety of other areas. A number of case histories will be presented.

9:10 AM

MECHANICAL EVALUATION THE POTSHELL OF THE HIGH AMPERAGE CVG-VENALUM CELL DURING START-UP: *Abrahan Rodriguez*[1]; Jaime Zarate[1]; [1]CVG-Venalum, Gerencia de Investigación y Desarrollo, Estado Bolivar VENEZUELA

During the start up, the potshell of the V-350 cell experiences large deformations mainly due to thermal loads. These deformations have a considerable influence on the subsequent performance of the cell during its operation. Hence, the capacity of predicting the relationship between the start up process and the state of stress and deformation that the potshell undergoes is desirable. In order to do this, a structural model, based on the finite elements method was developed, using the commercial code ANSYS. The model comprises 3D analysis, taking into account a quarter of the cell, using shell and brick elements. The nolinearity of the material properties was considered by means of an elastophastic analysis. A comparison between experimental results and those from the model, which is indicates a good agreement.

9:30 AM

CVG-VENALUM HIGH AMPERAGE SMELTER REDUCTION CELL, SOME OPERATING RESULTS: *Jesùs Alvarez*[1]; Carmen Castillo[1]; [1]C.V.G. Venalum, Investigación y Desarrollo, Ciudad Guayana, Estado Bolivar Venezuela

A high amperage smelter reduction cell has been designed by CVG-Venalum to operate at an amperage from 320 to 350 kA. The promising operating results achieved at 320 kA show the high potential of the cell design. Currently the cell design is under an optimization process in order to maximize current efficiency and minimize energy and raw material consumption and also investment costs. The optimization process is carried out by experimental tryouts and computer models. The results of the prototypes operating at an average amperage of 320 kA are discussed in this paper.

9:50 AM Coffee Break in Exhibit Hall

10:00 AM

ELECTRODEPOSITION OF INDIUM PHOSPHIDE: *S. Gueijman*[1]; C. Schvezov[1]; A. Lamagna[1]; [1]University of Misiones, FCEQyn, Misiones Argentina

Indium Phosphide was electrodeposited from aqueous solutions containing Phosphorus and Indium compounds using a galvanostatic technique. The materials employed as substrates include titanium foil, graphite, silicon electronic and metallurgical grades and fluorine doped tin oxide conducting glass. Thin films were obtained on all substrate materials. The thickness varied from 0.1 to 4.0 micron. The thickness is shown to depend linearly with deposition time at constant current density and constant temperature. It was also observed the deposition of small isolated crystals in denuded areas. The technique as well as the results are presented and discussed and possible reaction mechanisms are proposed.

10:20 AM
THE SIEMENS PROCESS OF POLYSILOCON PRODUCTION: NUCLEATION & GROWTH ABOUNDS: *James A. Gordon*[1]; [1]Advanced Silicon Materials, Inc., Moses Lake, WA 98837 U.S.A.

With the exception of growing industry demand for new fluid bed technology, the process developed by Siemens still stands as the most prominent venue by which the bulk of the world's semiconductor grade (SG) polycrystalline silicon (poly) is produced. ASiMI is the world's only producer of Siemens poly using silane, SiH_4; the rest of the world's Siemens poly producers use trichlorosilane, $SiCl_3H$. Recent world demand for silicon use in integrated circuits has skyrocketed and brought enhanced focus to poly's segment in the "silicon production chain". The following paper gives a brief review the ASiMI's unique twist on the process developed by Siemens. The paper discusses in greater detail silicon's nucleation and growth characteristics governing CVD processes as they relate to: ASM/TMS's 1994 Materials Week Conference symposium entitled "Defect Structure, Morphology and Properties of Vapor & Electro deposits". It also discusses the more recent work published by A.W. Tiller entitled "The Science of Crystallization: microscopic interfacial phenomena".

10:40 AM
PARTICLE STABILIZED METAL FOAM: *Dr. Sai Wai Ip*[1]; [1]University of Toronto, Metallurgy and Materials Science, Toronto, Ontario M5S 3E4 Canada

A low temperature analog and a high temperature system have been designed and developed to investigate the effect of solid particles on the stabilization of aluminum foam. The foam stability was evaluated using the average foam life. The effect of wettability, particle size, and concentration of SiO2 particles have been investigated at various gas flow rates in the low temperature analog. The results indicated that only silica particles with suitable wettability can stabilize liquid foam. Foam stability increases with decreasing particle size and increasing particle concentration. The effect of SiC particle concentration and temperature on aluminum foam stabilization were investigated in the high temperature system. Aluminum only starts to foam when a critical concentration of SiC is present, and above the critical concentration, the obtained foam height increased with increasing concentration of SiC particles.

11:00 AM
POROUS METAL TECHNOLOGIES FROM UKRIANE: *Dr. Timothy J. Langan*[1]; David K. McNamara[1]; Brian Gable[1]; Sergei Pan[1]; Vitaly A. Pereloma[1]; Yurii P. Lenda[1]; [1]Ashurst Technology Center, Baltimore, MD 21227 US

Ashurst Technology Corporation is currently evaluating and commercializing a number of porous metal technologies developed in Ukraine. The three principal approaches for fabricating porous metal products which we are currently developing include: 1) "powder metal" processes, 2) a novel casting process and 3) a novel rapid deposition process. Porous metal products have been fabricated using these techniques for alloy systems ranging from aluminum to titanium to nickel based superalloys. Key aspects of each technology will be discussed and defined, specifically focusing on the tradeoffs between cost, porosity level and performance. As part of this development effort Ashurst Government Services, a member company of the Ashurst group of companies, is participating in the Ultralight Metals program sponsored by DARPA/ONR. Our participation in this program is focused on the evaluation of the novel process for casting of porous titanium and titanium alloys. This process is used to fabricate titanium castings with solid outer skins and porous cores. Castings have been produced with porosity levels in the core that range from 20 to 70%. The microstructure and mechanical properties of these castings will be discussed.

GENERAL RECYCLING OF NON-FERROUS METALS: General Recycling I - Aqueous Processes

Sponsored by: Extraction & Processing Division, Light Metals Division, Recycling Committee
Program Organizers: Courtney Young, Montana Tech, Metallurgical Engineering, Butte, MT 59701; John P. Pickens, Alumitech Inc., 10380 Route 43, Streetsboro, OH 44241

Tuesday AM Room: Plaza Room B
February 17, 1998 Location: Convention Center

Session Chair: Larry M Southwick, L.M. Southwick & Associates, Cincinnati, OH 45229, James W Evans, University of California - Berkley, Materials Science and Mineral Engineering, Berkeley, CA 94720-1760

8:30 AM Opening Remarks

8:35 AM INVITED
SPOUTED BED ELECTROWINNING IN THE RECOVERY OF ZINC FROM SCRAP GALVANIZED STEEL: *J. W. Evans*[1]; V. Jiricny[1]; A. Roy[1]; [1]University of California-Berkeley, Materials Science and Mineral Engineering, Berkeley, CA 94720

There is a growing need to process galvanized steel scrap from automobiles, etc., in order to remove the zinc coating that otherwise causes problems in remelting of the scrap in electric arc furnaces. One approach that has moved to the pilot plant stage is that of Metal Recovery Technologies, Inc. of East Chicago (MRI). That company leaches the zinc from the scrap with a sodium hydroxide solution. The leached and washed scrap scrap can then be returned to the steel industry. What is left is a sodium hydroxide/zincate solution which must be processed to recover the zinc and the NaOH. Presently, this is done by MRI using electrodeposition onto planar electrodes at moderate current density and the resulting zinc is in the form of fine powder which is hard to process into, say, zinc for galvanizing. MRI has supported an investigation of a novel electrode, the spouted bed electrode (SBE), for zinc electrodepostion. In laboratory cells, zinc particles with low porosity have been grown up to 3mm in size. Microanalys is of the deposited zinc showed low levels of impurities. DC energy consumption values were usually in the range 2-2.5 kWh/kg which is well below the energy consumption of the existing cells (and of present-day cells for electrowinning from acid sulfate electrolytes). These results were achieved at current densities (few thousand A/m2) that are much higher than possible with conventional electrodes. Discussion is provided of the scale-up of the cell to a commercial cell.

9:00 AM
EXPERIMENTAL METHOD FOR DIRECT ELECTROREFINING OF BOTH COPPER AND COPPER ALLOY SCRAP: *Carla Lupi*[1]; [1]Universita Degli Studi di Roma, Dipartimento di ICMMPM, Roma 00184 Italy

The electrorefining of primary copper is a well known technology: in this work, copper scrap was directly processed in the same manner. The copper and copper alloy scrap was previously pressed by means of a 20 ton apparatus in order to avoid pyrometallurgical operations. The samples obtained in this manner showed a good compactness so that they were used as anodes in the studied elctrorefining process. The tests were carried out on anodes made of copper scrap, copper alloy scrap,

and a mixture of the two. The electrorefining tests were performed at both 303 K and 333 K, in a perspex cell having a volume of 500 ml using a current density of 250 A/m2. The cathode used was always a sheet of pure copper and the electrolyte composition was 40-50 g/l Cu as CuSO4 and 150-200 g/l H2SO4. The current efficiency in the range of 90-92% and a specific consumption ranging from 0.17-0.21 kWh/kg of copper were reached in all tests. The refined copper deposits were analyzed by AAS to verify their purity and observed by SEM to highlight their morphology.

9:25 AM INVITED

ACID-BASED PROCESS FOR REMEDIATION OF LEAD FROM CONTAMINATED FIRING RANGE SOILS: *M. Misra*[1]; D. Halbe[2]; M. Nay[3]; [1]University of Nevada - Reno, Chemical and Metallurgical Engineering, Reno, NV 89557; [2]Consultant, Salt Lake City, UT 84108; [3]BDM International, Inc., Albuquerque, NM 87106

Extensive amounts of particulate and dissolved lead species are present throughout the Army firing ranges of the Department of Defense sites. The removal of lead from the contaminated soils of Fort Polk, Louisiana, was successfully accomplished in a pilot test program by acid dissolution and precipitation. This paper describes the nature of the lead distribution, solution chemistry and precipitation kinetics, and recirculation of acid lixivant in a closed loop system.

9:50 AM Coffee Break in Exhibit Hall

10:05 AM INVITED

RECOVERY AND RECYCLING OF LEAD FROM SMALL-ARMS RANGE SOILS: *Eric Drescher*[1]; Arun Gavaskar[1]; Dan Janke[1]; Barbara Nelson[2]; [1]Batelle, Columbus, OH 43201; [2]Naval Facilities Engineering Service Center, Port Hueneme, CA

Heavy metals recovery via physical separation and acid leaching was demonstrated at Fort Polk, Louisiana on a small-arms range. This range was typical of the over 2600 United States Department of Defense Installations used for training exercises. The soil contained high concentrations of particulate, as well as adsorbed lead and copper. Conventional range maintenance activities have consisted of excavation and off-site landfill disposal, or on-site stabilization of the range soil. Fresh soil is then used as backfill for continued operation of the range. By utilizing mining industry techniques, such as physical separation/acid leaching, the lead and the other metals in the soil can be recovered and sent to an off-site smelter for recycling. The physical separation/acid leaching technology employs equipment used for mineral beneficiation in the mining industry. The recovery of the particulate metals at Fort polk was achieved by size and density separation. Vibrating screen decks and spiral classifiers were used to separate the fines from the coarse soil. A jig was used to remove particulate metals from the coarse soil. Acid washing of the fine soil with a weak or a strong acid was used to recover the adsorbed metal species. After the lead had been dissolved into solution precipitating agents and flocculants were used to recover the metal species from the solution as a precipitate. The precipitate sludge that was generated from the operation was dewatered and sent to an off-site smelter for recycling. By using this technology, over 30,000 ponds of metal was recovered and recycled from 1300 tons of range soil. Additionally, the processed soil was returned and reused in the active small-arms range.

10:30 AM

THE EXTRACTION OF METALS FROM INDUSTRIAL HAZARDOUS WASTES AND THE PRODUCTION OF A NON-HAZARDOUS RESIDUE: *Luis W. Pommier*[1]; [1]ISO, Inc., Rancho Santa Margarita, CA 92688

The industrial wastes generated by the plating industry, the circuit board manufacturing industries and other related industries normally contain high concentrations of metals, which makes them hazardous. The extraction of the contained metals and their separation may be achieved by both pyro and hydro metallurgical processes. Some of the industrial wastes, those rich in some metals like nickel, for instance, are being treated like mine ore concentrates and are being fed to smelting furnaces. The slage from these smelter operations are hazardous; they have, however, special environmental dispensations issued by the regulatory authorities. Hydrometallurgical processes have been reported; they also generate a residue which is hazardous because not all the valuable metals are leached out and, also, because "non-valuable" components like chromium are less readily leached. Residues from the plating industry, containing nickel, copper, zinc, iron and chromium as the major constituents and also sodium and calcium, together with cadmium, cobalt, lead, manganese, magnesium, molybdenum, and potassium, have been processed for the extraction of the valuable components. The generation of electrolytic nickel, copper and zinc and also of ferric chloride and chromium oxide is reported. The operation is achieved by a caustic leach for the extraction of zinc, followed by a sulfuric acid leach for the extraction of nickel and copper. This acid leach also extracts the iron and some chromium. The leaching operations generate a residue, while small in volume compared to the initial feed, still contains traces of the valuable metals and a portion of the chromium which makes it hazardous. Additional leaching with hydrochloric acid or nitric acid is required for its complete dissolution. Neutralization with lime renders the chromium soluble in sulfuric acid for its mixture with the main leach liquor. The other minor constituents mentioned are present in concentrations each of less than 0.1% and are handled as impurities in the process. The metals which are soluble in the pH range between 0.5 and 2.0 concentrate in the leaching operation from where they are bled off. The others will concentrate on the raffinate from the solvent extraction operations from which they can be bled off. These bleeding streams are hazardous and the "impurity metals" are again present in concentrations which would make them valuable, however, the amount present is so small that they do not grant their processing. However, they could be marked to specialized smelters, both for their value and for the removal of the associated liabilities. The extraction of the valuable metals, of the hazardous constituents, the generation of a marketable mixture of minor constituents and the production of a non-hazardous residue for declassification is profitable achieved.

10:55 AM INVITED

RECYCLING ZINC RECOVERED FROM ELECTRIC ARC FURNACE DUST: IS THERE A BETTER WAY?: *Larry M. Southwick*[1]; [1]L.M. Southwick & Associates, Cincinnati, OH 45229

Steel mill electric arc furnace (EAF) dust is a RCRA listed hazardous waste and its treatment and/or disposal are regulated by a complex set of rules. These regulations were originally established to encourage recovery and recycling of valuable components. For EAF dust, the more valuable constituents include zinc, lead, cadmium and iron. In fact, current trends are in the opposite direction, as the regulations have complicated the ability to commercialize new treatment technologies and created substantial roadblocks and liabilities for processors. As a result, almost half of the EAF dust generated in 1997 will be land filled. The problems are compounded by difficult processing requirements, less than sterling examples of technology development and mechanical operating problems. This paper explores some options to simplify the processing requirements and thereby easing difficulties in commercializing new technologies and expediting the recycling of recovered metals. Dust processing usually includes a simple step followed by two complicated steps. The simple step is fuming of heavy metals away from iron and other residues. The complex steps are (1) separating and purifying the heavy metals and (2) upgrading the iron residue. The first complex step can be simplified by producing an intermediate product that is amenable to to processing by zinc refiners. This route benefits from the currently under-utilized (by dust processors) resource offered by refiners, who have experience in existing processes for separation and purification of zinc-based heavy metals. Various processes and their associated product options are reviewed and compared. Future directions for dust processing developments are suggested.

HARD COATINGS BASED ON BORIDES, CARBIDES & NITRIDES: SYNTHESIS, CHARACTERIZATION & APPLICATIONS: Session I

Sponsored by: Materials Design and Manufacturing Division, Surface Modification & Coatings Technology Committee
Program Organizers: Yip-Wah Chung, Northwestern University, Dept. of Materials Sci & Eng., Evanston, IL 60208; Ray W.J. Chia, Western Digital Corporation, 2109 Tasman Dr., Santa Clara, CA 95054; Ashok Kumar, University of South Alabama, Dept. of Electrical & Comp Eng., Mobile, AL 36688-0022

Tuesday AM Room: Centro Room C
February 17, 1998 Location: Convention Center

Session Chair: Yip-Wah Chung, Northwestern University, Department of Materials Science and Engineering, Evanston, IL 60208, M. Shamsuzzoha, The University of Alabama, Department of Metallurgical and Materials Engineering, Tuscaloosa, AL 35487

8:30 AM Welcome and Opening Remarks

8:35 AM
THE ONR PROGRAM IN NANOSTRUCTURED COATING TECHNOLOGY: *Lawrence T. Kabacoff*[1]; [1]Office of Naval Research, Arlington, VA 22217-5660

The office of Naval research funds research and development of thermal spray deposition of nanostructured materials for wear, erosion, cavitation, and thermal barrier applications. Under this program, extremely hard, highly adherent coatings of nanoscale Co/WC have been successfully fabricated. The synthesis and processing techniques, as well as results of mechanical testing will be discussed.

9:00 AM INVITED
DEPOSITION AND PERFORMANCE TESTING OF NANOSTRUCTURED MULTILAYERS: Henja Jensen[1]; Jaroslav Sobota[1]; *Gunnar Sorensen*[1]; [1]Aarhus University, Institute of Physics and Astronomy, Aahus C. DK 8000 Denmark

Coatings of nanostructured carbon nitride/titanium nitride multilayers have been deposited using a side by side target configuration. Mass-flow of nitrogen and voltages of the sputtering cathodes were used for process control. By selecting stable deposition points it was possible to obtain low friction coatings. Previously reported friction coefficients for titanium carbo nitrides are fairly large, but a C-N/TiN nanostructured system show for a Si_3N_4 ball reciprocating on a coating deposited at the point (A-high), where sputtering pressure exhibit a rise, a low friction coefficient of 0.1 was measured. The acoustic emissions scratch test was used for measuring the film adhesion, but also for characterization of the nanostructured system. Adhesion values based on optical observation showed typical values of 60 N, but for the A-high deposition point 100 N was obtained. Results on coating transfer to the ball will be communicated, and particularly for transfer to Si_3N_4 ball homologous to the crystalline C_3N_4 will be discussed.

9:25 AM INVITED
ABRASIVE AND EROSIVE WEAR BEHAVIOR OF WC-Co COATINGS PRODUCED BY HIGH ENERGY PLASMA SPRAY (HEPS): *J. A. Hawk*[1]; J. W. Simmons[1]; M. Scholl[2]; [1]Albany Research Center, U.S. Department of Energy, Albany, OR 97321; [2]Oregon Graduate Institute of Science and Technology, Portland, OR 97291

Thermally sprayed coatings are being increasingly used to reduce wear or modify friction in many sliding, abrasive and corrosive wear applications. Of these coatings, WC-Co offers many advantages in an aggressive wear environment. In this research, high energy plasma spray (HEPS) has been used to produce high-quality WC-Co coatings. Abrasive and erosive wear behavior of WC-Co coating produced using the HEPS technique have been determined at ambient conditions using erosion test methods. Elevated temperature (< 350°C) erosion tests have also been performed using both inert gas and steam as the abrasive particle carrying medium. The severity of the particle-coating interaction and the mechanisms of materials removal for each tribo-environment has been determined using scanning electron microscopy. Comparison with monolithic WC-Co and stellite coatings produced using HVOF will be made.

9:50 AM
THREE-BODY ABRASION OF WC-12%CO THERMAL SPRAYED COATINGS: A. C. Bozzi[1]; J. R.T. Branco[1]; *J. B. D. DeMello*[1]; [1]Universidade Federal, de Uberlandia Brazil

In this study, three-body abrasion resistance of 1020 annealed steel samples coated with WC-12%Co HVOF coatings was evaluated. The tests were performed using SiO^2, Al^2O^3 and SiC as abrasives and five levels of pressure ranging from 0.10 to 0.60 N/mm_2. The wear rate was evaluated after reaching the steady state of wear. The microstructural characterization of the coatings and their wear micromechanisms were performed using scanning electron microscopy. The results show that the abrasion resistance depends strongly on the abrasive hardness. The cohesion strength between lamella is critical to abrasive resistance in severe conditions. The effect of the normal force on the wear rate depends on the nature of the abrasive used.

10:10 AM Coffee Break in Exhibit Hall

10:25 AM
MATERIALS PROCESSING FOR HEAVY MANUFACTURING: A FOCUSED AREA IN THE ADVANCED TECHNOLOGY PROGRAM: *Clare M. Allocca*[1]; [1]National Institute of Standards and Technology, Gaithersburg, MD

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 ATP enables industry to pursue promising technologies that otherwise would be ignored or developed too slowly to compete in rapidly changing world markets. In the highly competitive, fast-moving international marketplace, the ATP creates opportunity. This presentation will concentrate on current progress in one specific focused area of ATP: Materials Processing for Heavy Manufacturing. The intent of this program is to develop and demonstrate cost-effective and innovative materials processing technologies that will help U.S. heavy manufacturing companies, in the markets of automotive powertrain/engine/chassis, heavy equipment, and stationary power generation, make longer lasting, more reliable, and more efficient products. Not only do these markets deal with common components, such as engines, power transmission machinery, and highly-loaded structures, but in the fabrication of components for these areas, there are overlying materials processing issues that drive the markets for these components. The scope of this program is limited to materials processing projects in ceramics, metals, and their composites and coatings, which address the process areas of surface engineering, net-shape(and near-net shape) processing, and joining.

10:50 AM INVITED
EFFECTS OF ION ASSISTED PHYSICAL VAPOR DEPOSITION PROCESSES ON COATING ADHESION AND STRUCTURE: *J. M. Rigsbee*[1]; [1]University of Alabama at Birmingham, Department of Materials and Mechanical Engineering, Birmingham, AL 35294

Physical vapor deposition (PVD) processes usually are based on evaporation or sputtering mechanisms and the resulting thin film coatings have a very wide range of applications from microelectronics to machine tools. Relatively recently it has been recognized that additions of energy to growing thin films can significantly affect the film's adhesion, density and crystal structure, which are critical parameters governing coating performance. Ion assisted PVD processes typically involve bombardment of a growing film with plasma-generated ions and energetic neutrals with energies in the 10-500 eV range. This

addition of energy at the atomic-level serves to increase film adhesion and density and can in some circumstances actually alter the crystal structure of the deposited film. This presentation reviews current developments in ion assisted PVD processes and their applications. A cross-section TEM study of evaporated metallic films deposited with ion bombardment onto ceramic substrates demonstrates how ion assisted deposition reduces porosity within the coating and promotes adhesion by the formation of a chemically mixed interfacial layer. A study of reactively sputter deposited zirconia and yttria-stabilized zirconia films produced with various levels of applied substrate bias provides an example of the effects of ion bombardment on phase stability.

11:15 AM

RELATIONSHIPS BETWEEN ATOMISTIC BONDING AND INTRINSIC MACROSCOPIC HARDNESS: *C. R. Krenn*[1]; J. W. Morris, Jr.[2]; Seung-Hoon Jhi[3]; Jisoon Ihm[3]; [1]Lawrence Berkeley National Laboratory, Center for Advanced Materials, Berkeley, CA; [2]University of California, Department of Materials Science and Mineral Engineering, Berkeley, CA 94720; [3]Seoul National University, Department of Physics, Center for Theoretical Physics Korea

Recent advances in the fundamental theory of bonding in solids and advances in computer hardware and computational techniques have produced more accurate predictive models of atomistic material properties. However, clear functional relationships between intrinsic bulk hardness and both atomistic properties are not yet entirely apparent. Several previously published relationships between bulk hardness and both atomistically calculated and experimentally measured elastic properties and lattice energies are compared and contrasted. In metallic carbides and nitrides of the NaCl structure, hardness is found to scale more directly with the elastic shear modulus than with bulk modulus. New calculations of the elastic properties of TiC_xN_{1-x} for x = {0.0, 0.25, 0.5, 0.75, 1.0} are also presented. This work was supported by the USDOE under contract no. DE-AC03-76SF00098.

11:40 PM

FRACTURE TOUGHNESS PROPERTIES OF BORIDE LAYERS OF SOME BORONISED COLD WORK TOOL STEELS: Ugur Sen[1]; *Fevzi Yilmaz*[2]; [1]Sakaraya University, Casting Department, Adapazari 54188 Turkiye; [2]Sakarya University, The Department of Metallurgy, Adapazari 54040 Turkiye

We investigated that the fracture toughness properties of boride layers of two borided cold work tool steels. Boriding was carried out in salt bath consisting of borax, boric acid, ferro-silicon and aluminum. Boriding temperature of salt bath was 850°C and 950°C and boriding time was changing 1-8 hours. The presence of boride phases was obtained by x-ray diffraction. Hardness and fracture toughness was measured via Vickers indentation. It was also increasing of boriding time and temperature results the decreasing fracture toughness. Metallographic examination showed that boride layer of cold work tool steels were homogenous and flat on the surfaces of cold work tool steels.

HIGH TEMPERATURE SUPERCONDUCTORS: Bi-2212 and Y-123 Superconductors

Sponsored by: Jt. Electronic, Magnetic & Photonic Materials Division/ Structural Materials Division, Superconducting Materials Committee
Program Organizers: U.Balu Balachandran, Argonne National Laboratory, 9700 S. Cass Ave. Bldg. 212, Argonne, IL 60439; Pradeep Haldar, Intermagnetics General Corp., 450 Old Niskayuna Rd., Latham, NY 12110; Paul McGinn, University of Notre Dame, Center for Materials Science, Notre Dame, IN 46556

Tuesday AM Room: Fiesta C
February 17, 1998 Location: Convention Center

Session Chair: H. Kumakura, Natl. Res. Inst. for Materials, Sengen, Ibaraki 305 Japan

8:30 AM INVITED

GRAIN BOUNDARY STRUCTURE AND CRITICAL CURRENT DENSITY IN Bi-2212/AG TAPES: *Dr. H. Kumakura*[1]; Dr. H. Fujii[1]; Dr. K. Togano[1], [1]National Research Institute for Metals, Ibaraki 305 Japan

Grain boundary observations of c-axis grain oriented Bi-2212/Ag thick films were performed using high-resolution electron microscopy. The samples were prepared by a melt-solidification method under oxygen partial pressures P_{O2} from P_{O2} = 0.01 to 1.0 atm applying a dip-coating method. The most frequently observed grain boundaries were (001) twist boundaries. At the twist boundaries, amorphous phase with several nanometer thickness was occasionally observed. The population of twist boundaries as a function of a misorientation angle was investigated. When the misorientation angle corresponds to high-energy misorientation angle with low lattice coincidence, the twist boundaries tend to have amorphous layers. We found that the population of grain boundaries having amorphous phase decreased with increasing oxygen partial pressure during the heat treatment. The increase of transport J_c values of the films with increasing P_{O2} during the heat treatment can be understood in terms of the change of this grain boundary structures.

8:50 AM

EFFECTS OF NANOPHASE MGO ADDITIONS ON THE PROPERTIES OF $Bi_2Sr_2CaCu_2O_X$: *Dr. W. Wei*[1]; Dr. J. Schwartz[1]; Dr. K. C. Goretta[2]; Dr. U. Balachandran[2]; Dr. A. Bhargava[3]; [1]Florida State University, National High Magnetic Field Lab., Dept. of Mechanical Engineering, Tallahassee, FL 32310 USA

A serious limitation to applications of $Bi_2Sr_2CaCu_2O_x$ is weak flux pinning above 20 K. Improved flux pinning may also increase J_c at low temperature in high magnetic fields. One effective method to improve the magnetic behavior is to trap very fine nonsuperconducting phases within the 2212 grains. Nanosize MgO particles were added to the $Bi_2Sr_2CaCu_2O_x$ powder with varying molar fractions. Bulk samples and Ag-sheathed tapes were made from the Bi2212/MgO powder and heat treated by partial melting processing. Scanning electron microscopy and X-ray diffraction analysis were used to study the phases presented in the samples. The effects of the MgO additions on the flux pinning behavior were investigated by magnetic characterizations at various temperatures and fields.

9:10 AM INVITED

PROCESS OPTIMIZATION FOR AG-SHEATHED Bi-2212 SUPERCONDUCTORS: *Dr. Dah-Wei Yuan*[1]; Dr. Jan Kajuch[1]; [1]Concurrent Technologies Corporation, Johnstown, PA 15904 USA

The powder-in-tube (PIT) process has been widely used to fabricate long lengths of superconducting wires and tapes. However, it has been

noted that the performance of the superconductors over long lengths is inconsistent and difficult to reproduce. To help pinpoint the source of these inconsistencies, work was conducted to systematically study the effect of processing variables, including deformation and heat treatment procedures, on the electrical properties of the Bi-2212 tapes at cryogenic temperatures. In addition, the effect of varying powder particle sizes was examined. For tapes fabricated by different thickness reduction schedules, significant variations in critical current density (J_c) were observed. It is concluded that a combination of small roll diameter and small reduction-per-pass produces tapes with optimum J_c. Moreover, it was found that J_c was only optimized at a very narrow temperature range when melt processing was employed in a pure oxygen atmosphere. Microstructural examination revealed the correlation between J_c and volume fractions of a non-superconducting second phase and porosity.

9:30 AM INVITED

BiSrCaCuO-2212/Ag COMPOSITE CONDUCTORS: PROCESSING, PROPERTIES, AND POTENTIAL APPLICATIONS: *Dr. Kenneth R. Marken*[1]; Dr. Weiming Dai[1]; Dr. Seung Hong[1]; [1]Oxford Instruments, Carteret, NJ 07008-0429 USA

Many of the challenges of processing conductors based on the 2212 phase of BiSrCaCuO stem from the melt processing that is typically applied to these materials. Some problems include reactivity of the melt, density change, evolved oxygen, and carbon-dioxide formation. At the same time, melt processing in the presence of a silver matrix promotes formation of large, well-aligned grains, which enables high current density, particularly at low temperature and high fields. Methods of surmounting the challenges of conventional melt processing include carbon removal, control of heating rates, and temperature uniformity. Alternative thermal processes such as isothermal or continuous heat treatments offer advantages and disadvantages. Recent critical current densities attained in 2212/Ag composites will be presented. Potential applications of these conductors include high field magnet inserts, conduction cooled magnets, power transformers, and current leads.

9:50 AM INVITED

IMPROVEMENT OF FLUX PINNING CENTRES IN MELT PROCESSED Bi-2212/Ag TAPE: *Dr. Judith L. MacManus-Driscoll*[1]; Ms. Alice L. Crossley[1]; Dr. A. David Caplin[1]; [1]Imperial College of Science Technology and Medicine, Department of Materials, London, England SW7 2BP UK

In the Bi-Sr-Ca-Cu-O superconductors there has been considerable success in overcoming weak link problems, and at high temperatures intra-grain flux motion is thought to be the dominant dissipation mechanism. The microstructural and electrical homogeneity of Bi2Sr2CaCu2O8+d tape (Bi-2212/Ag) provides a good basis to study the effects of doping and secondary phase precipitates on flux pinning in a polycrystalline melt-processed system. In this study the complex Bi-2212 phase diagram has been used to quantitatively introduce secondary phase precipitates and magnetization measurements taken in order to assess their effects on pinning within the grains of the Bi-2212. In addition to this, the effect of additional doping on flux pinning within the grains has been investigated.

10:10 AM Coffee Break in Exhibit Hall

10:20 AM INVITED

HIGH CRITICAL CURRENT DENSITY YBCO TAPES USING THE RABITS APPROACH: *Amit Goyal*[1]; [1]Oak Ridge National Lab, Metals & Ceramics, Oak Ridge, TN 37831 USA

Epitaxial $YBa_2Cu_3O_x$ (YBCO) films with transport critical current densities of 0.5-3 x 106 A/cm2 (77K, 0T) were fabricated using laser ablation on various configurations of rolling-assisted-biaxially-textured-substrates (RABiTS). The field dependences are better than that for epitaxial YBCO films on single crystal substrates since a higher density of defects is present. The configuration of the highest Jc sample was YBCO (~0.2 mm) / YSZ (0.7 mm) / CeO_2 (0.0.05 mm) / Ni (125 mm). The CeO_2 and YSZ buffer layers were deposited using electron-beam evaporation and sputtering respectively. Both of these techniques are considered to be industrially scaleable. Efforts are underway to grow thicker films suitable for practical applications. In addition, advances made in the general areas of substrate fabrication including textured metal fabrication and buffer layer deposition will be discussed. Collaborative activities with the industry aimed at fabrication of long lengths using this approach will also be summarized.

10:40 AM INVITED

NON-VACUUM BASED ROUTES TO IN-PLANE ALIGNMENT OF YBCO FILMS: *Dr. Stuart Abell*[1]; Dr. Trevor Shields[1]; Dr. Tim Button[1]; Dr. Wolfgang Haessler[2]; Dr. Gunther Riesse[2]; [1]Birmingham University, Metallurgy and Materials, Birmingham B15 2TT UK; [2]IFW, Dresden Germany

The potential for the fabrication of YBCO films on technical substrates by non vacuum based techniques for high critical current and microwave power handling applications has been studied. Several approaches to obtaining some degree of bi-axial alignment in YBCO films deposited onto textured metallic and ceramic substrates have been investigated. The deposition routes include screen printing, doctor blading, dip coating, sol-gel and dip pyrolysis. Deposition on single crystal ceramic substrates of YSZ, STO and MgO has been compared with that on textured metallic substrates including Ag, AgCu and AgPd. The influence of heat treatment regime on the development of in-plane texture has been studied. The potential for these techniques to be adapted for scaling up and for coating three dimensional structures will be discussed.

11:00 AM INVITED

MAGNETIC LEVITATION WITH HTSC THIN FILMS: *Dr. T. H. Johansen*[1]; Dr. A. B. Riise[1]; Dr. H. Bratsberg[1]; Dr. Y. Shen[2]; Dr. V. Vase[2]; [1]University of Oslo, Dept. of Physics, Condensed Matter Physics, 0316 Oslo Norway; [2]NKT Research Center, DK-2605 Brondby Denmark

While experiments on magnetic levitation with high-temperature superconductors (HTSCs) are widely reported for bulk samples, the capability of HTSC thin films to levitate permanent magnets (PMs) is much less recognized. We report here measurements of levitation force, magnetic stiffness and temporal relaxation in systems of YBCO films and NdFeB PMs. The magnetic behavior of the films was also investigated by magneto-optical imaging. The observed results are discussed in terms of recent theories for thin type-II superconductors in transverse magnetic fields. A quantitative modelling of the behavior is presented. In particular, it is shown that measurements of the levitation force as function of the PM-HTSC distance represent a simple and precise method to determine the critical current density and its field dependence.

11:20 AM

THE GROWTH OF Bi-Sr-Ca-Cu-O SINGLE CRYSTAL WHISKERS: *Mr. Shriram Ramanathan*[1]; Dr. Maria Mironova[1]; Professor Krishnaswamy Ravi-Chandar[1]; [1]University of Houston, Department of Mechanical Engineering, Houston, TX 77204-4792 USA

Superconducting whiskers of Bi-2212 have been grown by a melt-quench process. Suitable raw materials of Bi_2O_3, $SrCO_3$, $CaCO_3$, CuO were melted in an alumina crucible at 1150°C and held there for about 30 minutes. The melt was poured onto a copper plate and pressed with a copper plate to get an amorphous plate. This amorphous precursor plate was subsequently subjected to different heat treatment cycles to study the recrystallization, phase formation and growth of the whiskers. Also, pellets were made by crushing the plates into a powder and pressing at different pressures and subjected to similar heat treatment cycles. These samples were studied extensively by differential thermal analysis, X-ray diffraction and scanning electron microscopy techniques to study the crystallization sequence leading to the growth of the whiskers. To understand the mechanism of growth of the whiskers, the recrystallized plate containing the roots of the whiskers were examined using cross-sectional transmission electron microscopy. The roots of the whiskers were identified and the various phases near the whisker root were identified by diffraction and energy-dispersive spectra. Defects present in the whisker root were also analyzed. In this presentation, the formation of the phases and the growth mechanism of the whiskers will be discussed.

11:40 AM INVITED

THE ROLE OF NANOSCALE PARTICLES IN BSCCO 2212 BULK POWDER AND TAPES: *Dr. A. Bhargava*[1]; Dr. J. Schwartz[2]; [1]University of Queensland, St. Lucia, Qld 4072 Australia; [2]National High Magnetic Field Lab., Florida State University, Tallahassee, FL 32310

$Bi_2Sr_2CaCu_2O_{8-x}$ has high critical current density at high magnetic field and low temperatures and can be fabricated into tapes with relative ease. In spite of several successes in melt texturing, practical limitations remain due to poor flux pinning at higher temperatures. It is widely believed that flux pinning can be improved by introducing various types of defects into the superconductor and that the defects must be very fine. Nanoscale second phase particles, such as Al_2O_3, C, TiO_2, MgO, and BaO, can be trapped within the superconductor structure and improve flux pinning. Nanoscale MgO, made by different chemical methods, is used to investigate the effect of second phase particle morphology on J_c. It is found that a high surface area MgO, made by delayed-gel method, provides the maximum increase in J_c for both bulk specimens and tapes of 2212.

HUME ROTHERY AWARD FOR PROF. RYOICHI KIKUCHI: Hume-Rothery Symposium III

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

Program Organizers: Juan M. Sanchez, The University of Texas, Center for Materials Science, Austin, TX 78712; Lawrence Anthony, The University of Toledo, Dept. of Physics and Astronomy, Toledo, OH 43606

Tuesday AM Room: 104
February 17, 1998 Location: Convention Center

Session Chair: Mark D. Asta, Sandia National Laboratories, Computational Materials Science, Livermore, CA 94551-0969

8:30 AM INVITED

APPLICATION OF THE CVM TO WAVE-NUMBER DEPENDENT SUSCEPTIBILITY FOR KDP-TYPE FERROELECTRICS: *Dr. Koh Wada*[1]; Dr. Y. Ogawa[1]; Dr. Y. Ihara[1]; [1]Hokkaido University, Division of Physics, 060 Sapporo, Hokkaido, Japan

The cluster variation method (CVM) is applied to a pseudo-spin Ising Hamiltonian of the Slater-Takagi model for KDP(KH_2PO_4)-type hydrogen-bonded ferroelectrics to calculate the wave-number dependent susceptibility. After a Landau-Ginzburg variational free energy in an inhomogeneous electric field is constructed, the susceptibility is derived as the linear response to the wave-number dependent electric field from an equation of state obtained as the thermodynamic equilibrium condition. A strong suppression of fluctuations along the easy (z) axis is shown to appear as the limit of ice-rule characteristic of ice-crystal is approached. The present result agrees with that of Havlin et al. and reproduces the result of neutron diffraction experiments in the para-electric phase. Moreover, the present calculation for the wave-number dependent susceptibility can be extended to the ferroelectric phase by utilizing the analytical result of the spontaneous polarization in the same approximation as that of paraelectric phase.

9:00 AM INVITED

EXPERIMENTAL AND THEORETICAL STUDY OF THE TEMPERATURE AND CONCENTRATION DEPENDANCE OF THE SHORT-RANGE ORDER IN Pt-V ALLOYS: Dr. David Le Bolloc'h[1]; Dr. Rene Caudron[2]; *Dr. Alphonse Finel*[2]; [1]Laboratoire Leon Brillouin, CEA-CNRS CE, Saclay, 91190 Gif sur Yvette, France; [2]Office National d'Etudes et de Recherches Aerospatiales, Direction des Materiaux, 92322 Chatillon Cedex, France

Recent experiments on the Pt-V system have shown that the effective pair interactions in this system are nearly concentration independent, despite a short range order intensity map that varies significantly with concentration. For the Pt_3V composition, the diffuse intensity shows maxima at k=(100), whereas, the diffuse intensity in Pt_8V displays a splitting around the (100) position, with incommensurate maxima. Our Monte Carlo simulations show that these two very different diffuse intensity map are well reproduced with the same interaction set with a dominant first neighbor interaction V_1. An Inverse CVM analysis in k-space confirm the previous results. Finally, we analyze the origin and behavior of the incommensurate split peaks in Pt_8V within a high temperature expansion and show analytically that the splitting is due to a large decrease of the influence of V_1 on the short range order as the concentration and/or the temperature decreases.

9:30 AM INVITED

CVM CALCULATION OF TERNARY PHASE DIAGRAMS: *Dr. Catherine Colinet*[1]; [1]LTPCM, UMR CNRS 5614, 38240 Saint Martin d'Heres, France

The cluster variation method (CVM) is one of the most efficient method for including short and long range order in the Gibbs energy calculation. Therefore the CVM is very important in computing phase diagrams specially in systems which display order - disorder transformations. In the present work isothermal sections in ternary systems of practical importance in alloy design problems have been calculated. The interaction terms have been obtained from available experimental data such as order - disorder temperatures, enthalpies of formation, phase boundaries or from theoretical calculations. In the Fe-Co-Al system, the calculation of the bcc phase diagram has been performed without introducing any ternary interaction term. In the Nb-Ti-Al system, literature results concerning ab-initio calculations have shown that the ternary effects are important. Therefore these interactions have been introduced in the CVM phase diagram calculation and their importance has been shown. The B2-A2 transition temperature and the probabilities of site occupations in the B2 phase for various compositions have been compared with recent neutron diffraction determinations. In the Fe-Co-Cu system the miscibility gap in the fcc domain has been calculated. At lower temperature the equilibrium between fcc and bcc phase has been investigated. Standard thermochemical lattice stabilities of the constituent elements are needed for this calculation. Magnetic interactions between nearest neighbors have been considered.

10:00 AM Coffee Break in Exhibit Hall

10:10 AM INVITED

ORDERING AND PHASE SEPARATION IN MULTICOMPONENT SYSTEMS WITH CHEMICAL AND MAGNETIC INTERACTIONS: *Cláudio Geraldo Schön*[1]; Gerhard Inden[1]; [1]Max-Planck-Institut für Eisenforschung, Düsseldorf D-40074 Germany

The Cluster Variation Method in the irregular tetrahedron approximation is applied to BCC systems with arbitrary number of components. Magnetic systems with arbitrary spin number are treated in the same way, each spin being equivalent to a component. Systems with chemical and magnetic interactions are considered. The interaction energy matrix includes tetrahedron interactions for the chemical part and pair interactions for the magnetic part of the Ising Hamiltonian. Several examples are given, illustrating the multicomponent aspects and the effect of both magnetic and chemical interactions in the calculation of phase diagrams.

10:40 AM

CLUSTER EXPANSION OF TERNARY Al-Cu-Ni ALLOYS: *Mathias Lars Ekman*[1]; [1]KTH, Theoretical Physics, Stockholm S-100 44 Sweden

The ternary alloy system Al-Cu-Ni has been studied with the use of cluster expansion. Due to the large size-mismatch, cell-internal and external relaxations are important. To deal with these, a reciprocal cluster expansion was performed. The structure inversion method (SIM) was used to extract effective cluster interactions. Enthalpies of formation, used as input in the SIM, were obtained through extensive ab initio full-potential calculations in the local density approximation of 49 ordered structures. Order-disorder transition temperature and the tem-

perature dependence of the site dependence of Cu in Ni3Al were studied through Monte Carlo simulations.

11:10 AM
THE SPIN S=7/2 FCC ISING FERROMAGNET: COMPARISON BETWEEN CLUSTER VARIATION METHOD AND MONTE CARLO CALCULATIONS: *Cláudio Geraldo Schön*[1]; Gerhard Inden[1]; [1]Max-Planck-Institut für Eisenforschung, Düsseldorf D-40074 Germany

Cluster Variation Method (CVM) and Monte Carlo (MC) calculations have been applied to model the thermodynamic properties of spin s=7/2 FCC ferromagnets with nearest neighbor pair interactions. The CVM calculations were made in the regular tetrahedron approximation and the MC calculations were performed in a $N=48^3$ computer crystal. The results of the internal energy, reduced magnetization and point probabilities for the spin species obtained with both methods are compared. The results obtained with the CVM are in surprisingly good agreement with the MC results in a large range of temperatures both below and above the Curie temperature, T_C. The CVM results for the internal energy differ only in a narrow range around T_C by less than 1% of the ground state energy.

11:40 AM INVITED
PHASE TRANSITIONS IN ISING SQUARE ANTIFERROMAGNETS: A COMPARISON OF THE MONTE CARLO SIMULATIONS AND DIFFERENT CVM APPROXIMATIONS: *Dr. E. Lopez-Sandoval*[1]; Dr. F. Aguilera-Granja[1]; Dr. J. L. Moran-Lopez[1]; [1]Universidad Autonoma de San Luis Potosi, Instituto de Fisica, San Luis Potosi, 7800 S.L.P., Mexico

The phase transitions occurring in the Ising square antiferromagnet with first- (J_1) and second- (J_2) nearest-neighbors interactions are studied as a function of the $V= J_2 /J_1$ parameter using the Monte Carlo Simulation (MC) method. Our simulation results base on the analysis of the magnetization at the critical temperature indicate that the system undergoes a second order phase transition for $V<0.5$ and a first order phase transition for $0.5 < V < 1.35$. Our results confirm a previous observation obtained using the Cluster Variational Method (CVM). Comparison of the MC results and different CVM approximations is done.

INTERNATIONAL SYMPOSIUM ON IRON ALUMINIDES: ALLOY DESIGN, PROCESSING, PROPERTIES & APPLICATIONS: Point Defects; Corrosion and Environmental Effects

Sponsored by: ASM International: Materials Science Critical Technology Sector, Flow & Fracture, Jt. Electronic, Magnetic & Photonic Materials Division/Structural Materials Divsion, Alloy Phases Committee, Materials Design & Manufacturing Division, Powder Metallurgy Committee

Program Organizers: S.C. Deevi, Philip Morris USA, Research & Development Center, Richmond, VA 23234; David G. Morris, University of Neuchatel, Inst of Structural Metallurgy, Neuchatel Switzerland; J.H. Schneibel, Oak Ridge National Laboratory, Metals & Ceramics Division, Oak Ridge, TN 37831; Vinod K. Sikka, Oak Ridge National Laboratory, Metals & Ceramics Division, Oak Ridge, TN 37831

Tuesday AM Room: 108
February 17, 1998 Location: Convention Center

Session Chairs: H. Neuhäuser, TU Braunschweig, D-38106 Braunschweig, Germany; J. H. Schneibel, Oak Ridge National Laboratory, Materials and Ceramics Division, Oak Ridge, TN 37381

8:30 AM PLENARY LECTURE
RECENT ADVANCES IN ALLOY DESIGN OF IRON ALUMINIDE ALLOYS: *C. T. Liu*[1]; E. P. George[1]; P. J. Maziasz[1]; C. G. McKamey[1]; J. H. Schneibel[1]; [1]Oak Ridge National Laboratory, Metals and Ceramics Division, Oak Ridge, TN 37831-6115 U.S.A.

Iron Aluminides based on FeAl and Fe_3Al possess excellent oxidation and corrosion resistance at elevated temperatures; however, their low tensile ductility and fracture resistance at ambient temperatures limit their use as structural material. For the past decade, considerable effort has been devoted to the understanding of brittle fracture at ambient temperatures and alloy design of such iron aluminides with improved properties using physical metallurgy principles. Moisture-induced environmental embrittlement, which has been identified as a major cause of poor ductility and brittle cleavage fracture in iron aluminides, can be alleviated by control of grain shape, grain size, surface condition, and alloy composition. Thermal vacancies can be easily induced in iron aluminides containing more than 40% Al, which strongly affect the yield behavior at ambient temperatures and yield-strength anomaly at elevated temperatures. Recent studies indicate that the impact toughness of FeAl can be dramatically improved by powder metallurgy through control of grain structure and boron addition. Also, highly wear-resistant iron aluminide composites containing WC, TiC, TiB_2, and ZrB_2 have been fabricated by liquid-phase infiltration methods. The effect of alloying additions on environmental embrittlement, fracture mode, defect structure, and impact properties of iron aluminides will be discussed. This research was sponsored by U.S. DOE, the Division of Materials Science; the Advanced Indu- strial Materials (AIM) Program; and the Fossil Energy AR&TD Materials Program under contract DE-AC05-96OR22464 with Lockheed Martin Energy Research Corp.

9:15 AM INVITED
VACANCIES, VACANCY AGGREGATES AND HARDENING IN FeAl: *M. A. Morris*[1]; O. George[1]; D. G. Morris[1]; [1]University of Neuchâtel, Institute of Structural Metallurgy, Neuchâtel Switzerland

It is well established that the presence of point defects can significantly affect the mechanical properties of intermetallic compounds. In

particular, the FeAl and NiAl systems with the B2 ordered structure have been confirmed to retain a high concentration of thermal vacancies during rapid quenching from elevated temperatures leading to significant increases in hardness. The excess vacancies can be eliminated by low temperature anneals leading to different softening processes that appear to depend on alloy composition and additions of ternary elements. The kinetics of hardening/softening processes that occur during high/low temperature anneals of different FeAl alloys have been studied. The low activation energies measured from high temperature anneals have been related to the mechanisms responsible for the increase in vacancy concentration retained by rapid quenching. TEM observations carried out from quenched specimens and at different stages during the low temperature anneals have helped elucidate the mechanisms responsible for the different vacancy elimination processes. The latter lead to incubation periods during which inhomogeneous distribution of <111> and <100> dislocations are observed.

9:45 AM INVITED

ON THE BORON EFFECT IN FeAl (B2) INTERMETALLICS: *Anna Fraczkiewicz*[1]; Anne-Sophie Gay[1]; Michel Biscondi[1]; [1]Ecole des Mines, Centre SMS, 42023 Saint-Etienne Cedex 2 France

Small boron additions are known to reduce the intergranular brittleness of some intermetallic, thanks to its intergranular segregation. Two different origins of this segregation were identified in FeAl (B2) alloys, containing 40 to 50 at. % Al. Its very fast kinetics, low level and almost no temperature dependence suggest a nonequilibrium mechanism, based on an interaction between boron atoms and the flux of migrating thermal between boron atoms and the flux of migrating thermal vacancies. Still, a low level (few % at. B) equilibrium segregation is also stable. In fact, no desegregation process was observed, even after a very long (three months) annealing. In the B-doped FeAl alloys, the kinetics of thermal vacancies migration is strongly accelerated compared to B-free alloys. As this effect is too strong to be explained only by intergranular phenomena, some other aspects of boron addition to FeAl alloys were also studied. In particular, clear differences in dislocation structures after annealing were observed between B-free and B-doped alloys.

10:15 AM Coffee Break in Exhibit Hall

10:35 AM INVITED

CRITICAL FACTORS AFFECTING THE HIGH-TEMPERATURE CORROSION PERFORMANCE OF IRON ALUMINIDES: *Dr. Peter F. Tortorelli*[1]; Dr. K. Natesan[2]; [1]Oak Ridge National Laboratory, Metals and Ceramics, Oak Ridge, Tennessee 37831-6156 U. S.; [2]Argonne National Laboratory, Argonne, Illinois 60439 Illinois

Iron aluminides are known to exhibit good-to-excellent corrosion resistance in a number of high-temperature environments. Under most conditions, this resistance derives from the ability of such alloys to quickly establish and maintain a sound and adherent alumina layer. This paper reviews the performance of iron aluminides under different aggressive high-temperature conditions and relates the results to fundamental metallurgical and environmental factors that control the development, adhesion, and durability of protective alumina. In this regard, the overall corrosion resistance depends not only on thermodynamic stability of the reaction product in a particular environment, and its growth kinetics, but also on scale integrity and morphology, the chemical and physical nature of the oxide-metal interface, alloy strength, and the specific composition of the iron aluminide. It is the interplay among these characteristics that determines the appropriate temperature range for long-term corrosion resistance in a particular environment. Despite the multiplicity of factors, a relatively simple lifetime prediction model, based on effects on aluminum consumption, can be used to evaluate the influences of changes in metallurgical parameters and to determine approaches to improving high-temperature corrosion resistance of iron aluminides. Research sponsored by the U.S.Department of Ener gy's Division of Materials Sciences and its Fossil Energy AR&TD Materials Program under contract DE-AC05-96OR22464 with Lockheed Martin Energy Research Corporation.

11:05 AM

CORROSION PERFORMANCE OF IRON ALUMINIDES IN MIXED OXIDANT ENVIRONMENTS: *K. Natesan*[1]; [1]Argonne National Laboratory, Energy Technology Division, Argonne, IL 60439 U.S.A.

Iron aluminide intermetallics are being developed for use as structural materials and/or as cladding for conventional engineering alloys. In addition to their strength advantages, these materials exhibit excellent resistance to corrosion in single- and multioxidant environments at elevated temperatures through the formation of slow-growing, adherent alumina scales. Corrosion resistance in a given environment is strongly dependent on the composition of the alloy and on the nature of the corrosive species prevalent in the service environment. Even though these intermetallics develop protective oxide scales in single-oxidant environments, the simultaneous presence of several reactants in the environment (typical of practical systems) can lead to the development of oxide scales that are nonprotective and undergo breakaway corrosion or to nonoxide scales that are detrimental to the performance of Fe-based intermetallics in environments that contain sulfur, carbon, chlorine, and oxygen and that are typical of development/breakdown, performance envelopes for long-term usage of these materials, approaches to modifying the surface of engineering alloys by cladding or coating them with intermetallics, and in-service experience with these materials. Research sponsored by the U.S. Department of Energy, Office of Fossil Energy, Advanced Research and Special Technologies Materials Program, Work Breakdown Structure Element ANL-4, under contract W-31-109-Eng-38.

11:25 AM

EFFECT OF WET ENVIRONMENT ON HARDNESS AND YIELD STRESS OF B2 FeAl ALLOYS: *Hideki Hosoda*[1]; Kyosuke Yoshimi[1]; Kanryu Inoue[2]; Shuji Hanada[1]; [1]Tohoku University, Institute for Materials Research, Sendai 980-77 Japan; [2]University of Washington, Department of Materials Science and Engineering, Seattle, WA 98195-352120 U.S.A.

Although many studies have been done on environmental embrittlement of Fe-Al alloys, very few have been done on the environmental effect of yield stress and hardness. In general, hardness and yield stress of Fe-Al alloys are believed not to be influenced or slightly reduced by a wet (hydrogen) atmosphere. Firstly, micro Vickers hardness (HV) changes were investigated for B2 FeAl alloys at room temperature as a function of the duration spent in (1) a wet environment at room temperature after a dry treatment, and (2) a dry environment at 427 K after a wet treatment. In the case of (1), hardness increases with the duration, then it reaches a maximum. By contrast, in the case of (2), hardness decreases with the duration and returns to an original value after the dry treatment. Hence, the hardness change is reversible between dry and wet environments. The hardness increment by the environments is about HV10. Secondly, the details were investigated through tensile tests using both Fe-Al poly and single crystals. A new method is proposed to estimate diffusivity (D) of a solute using relationships between hardness change and duration by taking into account the depth of the indenter. The D is estimated to be about 10^{-13} m^2/s, which is close to D of H in α-Fe if surface effects and/or lattice imperfections are considered. Environmental hardening of Fe-Al alloys is considered to be caused by solute hydrogen atoms absorbed from the wet atmosphere. Effect of ternary additions, Cr and Mn, on the environmental hardening was also investigated.

11:45 AM

THE HIGH-TEMPERATURE CORROSION OF Fe-28Al AND Fe-18Al-10Nb IN A $H_2/H_2S/H_2O$ GAS MIXTURE: *W. Kai*[1]; R. T. Huang[1]; S. H. Lee[1]; J. P. Chu[1]; [1]National Taiwan Ocean University, Institute of Materials Engineering, Keelung 20224 Taiwan, Republic of China

Iron aluminides (Fe3Al or FeAl) have been greatly considered for use as structural materials because of their excellent high-temperature oxidation resistance, relatively inexpensive material cost, and better strength-to-weight ratio. In this paper, the corrosion behavior of Fe-28Al and Fe-18Al-10Nb (at. %) in a $H_2/H_2S/H_2O$ gas mixture was investigated over the temperature range of 700 to 900°C. The effect of Nb addition on the corrosion behavior of the ternary alloy would also be

explored. In general, the corrosion kinetics followed the parabolic rate law although two-stage kinetics were noted in some cases. The steady-state parabolic rate constants increased with increasing temperature. Based on the equivalent addition (28 at. %) of alloying elements, it was found that Fe-18Al-10Nb exhibited lower corrosion rates than Fe-28Al by 2.1 to 4.5 orders of magnitude (depending on temperature). The scales formed on Fe-28Al consisted of mostly a-Al2O3 and FeS as well as a minor amount of FeAl2S4, while the scales formed on Fe-18Al-10Nb consisted of mostly α-Al_2O_3, Nb_3S_4, Nb_2O_5, and minor $FeNb_2S_4$ at T<800°C and of α-Al_2O_3, Nb_3S_4, and Nb_2O_4 at 900°C. The formation of Al_2O_3, Nb_3S_4, and Nb_2O_5 resulted in the reduction of corrosion kinetics of the ternary alloys. *Research sponsored by the National Science Council of Republic of China under Grant No. NSC 86-2216-E-019 002.

TUESDAY AM

INTERNATIONAL SYMPOSIUM ON PROCESSING OF METALS & ADVANCED MATERIALS: Microstructures and Properties

Sponsored by: Extraction & Processing Division, Synthesis, Control, and Analysis in Materials Processing Committee

Program Organizer: Ben Q. Li, Washington State University, School of Mechanical and Materials Engineering, Pullman, WA 99164-2920

Tuesday AM Room: 201
February 17, 1998 Location: Convention Center

Session Chair: Reza A. Mirshams, Louisiana State University, Baton Rouge, LA 70813 USA, Frank Ritzert, NASA Lewis Research Center, Cleveland, OH 44135 USA

8:30 AM

THE EFFECT OF ALLOYING ON TOPOLOGICALLY CLOSE PACKED PHASE INSTABILITY IN ADVANCED NICKEL-BASE SUPERALLOY RENE N6: *Frank Ritzert*[1]; David Arenas[2]; Dr. Vijay Vasudevan[3]; [1]NASA Lewis Research Center, Cleveland, OH 44135 USA

An investigation was conducted to describe topologically close packed (TCP) phase instability as a function of chemical content in advanced nickel-base superalloy Rene N6. TCP phases are detrimental to overall high temperature performance of nickel-base superalloys because of their brittle nature and because they deplete the nickel-rich matrix of potent solid solution strengthening elements. Thirty-three variations of polycrystalline Rene N6 determined from a design-of-experiment approach were cast and homogenized at 2400 °F for 80 hours followed by exposure at 2000°F for 400 hours to prompt TCP formation. The alloys had the following composition ranges: Co 10 to 15 weight %, Mo 0.5 to 20%, W 5.5 to 7%, Re 5.5 to 6%, Ta 7 to 8.5%, Al 5.5 to 6.25%, and Cr 3 to 5%. Physical and chemical characteristics of all microstructures obtained were described using various analytical techniques. A mathematical model of TCP occurrence (sigma and P phase) was generated for polycrystalline Rene N6.

8:50 AM

THE EFFECTS OF Ti AND Sr ON THE MICROSTRUCTURES OF Al-11.3WT%Si ALLOYS PRODUCED BY THE CONTINUOUS CASTING PROCESS : *M. H. Kim*[1]; H. H. Jo[2]; C. S. Kang[3]; C. R. Loper, Jr.[4]; T. S. Song[1], [1]Chungbuk National University, Dept. of Materials Engineering, Cheongju Korea

An investigation has been conducted to describe the effect of grain refiner or modifier such as Ti or Sr, respectively, on the microstructure of Al-11.3wt%Si alloys produced by the conventional continuous and the horizontal continuous casting process with the heated mold for obtaining unidirectional solidification at a high cooling rate (300°C/s~2000°C/s). Results showed that the addition of 0.02 %Si or 0.2-0.4%Ti promoted the directionality of primary a dendrite, whereas the addition of 0.6%Ti suppressed the directionality. Also, the addition of 0.02%Sr suppressed the occurrence of feathery grains, while the addition of 0.2%Ti promoted the occurrence of feathery grain. The addition of Ti over 0.4% suppressed the occurrence of feathery grain, resulting in the increased grain-refining effect. The addition of Ti also increased the coarsening effect of eutectic silicon phase in the Al-11.3wt%Si alloy.

9:10 AM

PROCESSING AND PROPERTIES OF HOT-PRESSED IN-SITU Al/(TiB2+Al203) METAL MATRIX COMPOSITES: *C.F. Feng*[1]; L. Froyen[1]; [1]Katholieke University Leuven, Department of Metallurgy and Materials Engineering, Leuven Belgium

In-situ processes have emerged as new and promising techniques for metal matrix composite fabrication. They offer significant technical and economic advantages over conventional processing. One of the in-situ processing routes that have been used is reactive free sintering of a mixture of powder reactants. However, materials synthesized via this route are always porous because of density difference between reactants and products, etc. An example is the porous Al/(TiB2+Al2O3) MMCs obtained by heating powder mixtures Al+TiO2+B with TiO2 and B in stoichiometric ratio for forming TiB2. In this study, the porous Al/(TiB2+AI203) composites were further processed by hot-pressing at ~ 600°C. This processing cycle was designed such that the composites could be densified. The green samples utilized in this study were obtained by cold pressing ball-milled powder mixtures. The thermal effects during the reactive processes were investigated by DSC. Variation of reaction temperatures was observed by changing the relative amount of Al in green samples. Besides, influences of cold-pressing pressures on DSC results were studied as well. The XRD analyses showed that the hot-pressed products consisted of Al, TiB2 and Al203- Properties of the products were assessed by microstructural characterization (LOM, SEM and EDS), microhardness, Young's modulus and bending tests. The results show that good microstructures, elastic properties and strengths as well as acceptable ductilities were achieved. For the composition 79.74wt% Al15.95wt% TiO2-4.31wt% B, after the reactive free-sintering and hot-pressing cycles, Young's modulus is 105 GPa, bending strength is 509 MPa and maximum strain is 5.0%; for composition 88.73wt% Al-8.87wt% TiO2-2.40wt% B, they are 89 GPa, 311 MPa and 8.2% respectively. It can be seen that the properties of products can be tailored by adjusting the relative amounts of reactants in green samples. Furthermore, for comparison reasons, Al and a binary system Al-TiO2 were identically processed as the ternary systems. Their microstructures and properties were studied.

9:30 AM

HIGH STRENGTH ALUMINUM MATRIX COMPOSITES REINFORCED BY NEWLY DEVELOPED α-ALUMINA SINGLE CRYSTAL PARTICLES: *Hiroshi Tabuchi*[1]; Akihiko Takahashi[1]; [1]Sumitomo Chemical Co., Ltd., Tsukuba Research Laboratory, Tsukuba, Ibaraki 300-32 Japan

High strength aluminum matrix composites were prepared and studied by using newly developed nearly mono-dispersed α-alumina single crystal particles each of which has a regular polyhedral shape as reinforcements. The composites were formed by centrifugal casting using aluminum casting alloys (Al-Si and Al-Cu-Mg) as the matrices and followed by heat treatment. The volume fraction of the alumina particles was as high as 60%. The same matrix composites reinforced by conventional crushed fused alumina particles were similarly prepared and investigated as the reference. The bending strength and tensile strength of the Al-Cu-Mg matrix composites reinforced by the novel alumina particles of 10 micron in average diameter are as high as 1020 MPa and 560 MPa, respectively, which are higher than those of the conventional alumina composites. Furthermore, the bending strength of the novel alumina composites degraded less than that of the conventional alumina composites after thermal fatigue tests. A number of cracks in the matrix seemed to influence the thermal fatigue properties since many cracks were observed in the conventional alumina composites, whereas only a few cracks were observed in the novel alumina composites. This was confirmed by an SEM observation on the sample composites before and after the thermal fatigue tests.

9:50 AM

STRUCTURE FORMATION OF REACTIVE SYNTHESIZED Al-TiB2 COMPOSITES: *H.J. Brinkman*[1]; J. Duszczyk [1]; L. Katgerman[1]; 0[1]Delft University of Technology, Laboratory of Materials Science, AL 2628 The Netherlands

Al-TiB2 are reactively synthesized from elemental powders. To obtain processing-structure relations for this emerging composite production technique the structure formation is investigated with a combination of DSC SEM and XRD techniques. The reaction sequence is identified with DSC and with use of the DSC the process is halted at various known stages in the process. Further investigation of intermediate reaction products is done with SEM and XRD. Reaction rate limiting sub processes are identified together with the influence of heating rate, composition, and alloying elements on the final structure of the composite product. Results of initial mechanical tests will also be presented.

10:10 AM Coffee Break in Exhibit Hall

10:30 AM

THERMAL ANALYSIS OF AGED BINARY AL-LI ALLOYS: *Sedat Ozbilen*[1]; [1]Gazi University, Faculty of Technical Education, Metal Department, Teknikokullar, Ankara Turkey

Al-Li binary alloys with nominal Li contents of 0.1, 1.0, 2.8 (in wt%) were aged naturally (for 3 months) and artificially (not only for both at 65% and 100°C but also for two days at 190°C) after water quenching to 25°C following solutionizing at 530°C for 20 minutes. Aging behavior of these binary alloys is studied by Vicker's Hardness measurements and DSC/DTA thermal analysis and the results of this investigation will be presented.

10:50 AM

THERMAL ANALYSIS OF Al-Cu-Mg-(Li) ALLOY SYSTEM: *Sedat Ozbilen*[1]; Muzaffer Erdogen[1]; [1]Gazi University, Fac. of Tech Educ., Metal Educ. Dept., Teknikokullar, Ankara Turkey

A series of ternary (Al-Cu-Mg) and quaternary (Al-Li-Cu-Mg) alloys are used to investigate their response to aging (natural and artificial) by thermal analysis. Rolled sheet samples are fully recrystallized after solution treatment at 803K for 1.2x103sec followed by water quench at 293K. Alloys are naturally aged for up to 5.18x106sec and are artificially aged at 463K for up to 1.73x105sec. By using a combination of DSC/DTA thermal analysis and Vicker's hardness measurements, their response of aging is studied.

11:10 AM

ELECTRICAL PROPERTIES OF MBE GROWN InSb AND SnTe DOPED InSb ON GaAS: *Mr. Thomas A. Rawdanowic*[1]; Dr. Jie Li[1]; Dr. Shanti Iyer[1]; Mr. Venkatraman Sreenivasan[1]; Dr. Ward J. Collis[1]; [1]North Carolina A&T State University, Electrical Engineering, Greensboro, NC 27411 USA

InSb being the lowest band gap material amongst the III-V semiconductors with low effective mass, has long attracted research interest, due to its potential application in far infrared devices and for high speed circuit element. In this paper, we report on the electrical characteristics of MBE grown InSb and Te-doping on (100) GaAs using SnTe source by Molecular Beam Epitaxy. A systematic study of the effect of growth conditions (over growth temperatures & V/III beam equivalent pressure (BEP) ratios) on the electrical & structural properties of InSb has been carried out. Substrate temperature was varied from 370°C to 420°C and BEP ratio was varied from 1 to 3. The as-grown epilayers are n-type in the temperature range of 10 K to 300 K investigated. Room temperature transport parameters are found to be relatively independent of both the growth temperature and BEP ratios varying from 1.6 to 3. The room temperature and 77 K mobility as high as 66,700 cm2/V-sec (1.9x1016 1/cm3) and 25,900 cm2/V-sec (1.5x10 15 1/cm3) has been obtained on 4-6 mm thick epilayers. The full width half maxima of the x-ray rocking curve obtained on these layers is typically in the range of 98 to 204 arc-sec. Systematic and detailed investigation of SnTe as a Te dopant source in InSb will also be presented.

11:30 PM

TEM STUDY OF TIB-REINFORCED NANOCRYSTALLINE TI-MMCS PRODUCED BY MECHANICAL ALLOYING.: *S. Ozbilen*[1]; [1]Guzi University, Fac of Tech. Educ., Metal Educ. Dept., Teknikokullar, Ankara Turkey

Mechanical alloying synthesizing technology is utilized to produce nanocrystalline Ti-MMCs reinforced by TiB intermetallic compound. MA?ed powders produced from TiH2 and B powders were examined by X-Ray Diffraction and SEM. All powders afterwards were annealed within DTA in Ar at temperatures of 650, 750, 850 and 1200oC for 3 minutes. Detailed XRD, SEM and especially TEM study of the samples are carried out to determine the location of dislocation densities in the microstructures of Ti-TiB MMC material.

11:50 AM

CORROSIVE WEAR STUDY ON COMPOSITES OF 2014 ALUMINUM ALLOYS : *Shane Andrews*[1]; Gustavo Vasquez[1]; S. K. Varma[1], [1]The University of Texas El Paso, Department of Metallurgical and Materials Engineering, El Paso, Texas 79968 USA

The composites of 2014 aluminum alloys reinforced with Al2O3 particles have been solutionized at 540°C for times ranging from 4 to 20 hours. The cylindrical electrodes of heat treated samples have been subjected to corrosive wear process in an electrolyte containing O.lM NaCl solution by impact and continuous scratching. The transient current generated from the composites containing different volume fractions of alumina particles have been compared with the those from the monolith alloys in a similarly heat treated condition. The morphology of scratches have been examined by SEM and microstructures near the scratches have been observed by a TEM. The role of dislocations generated from the coefficient of thermal expansion (CTE) effect and changes in grain size on the corrosive wear behavior will be evaluated. The results will be compared with the work earlier performed by this group on 6061 aluminum alloy and composites reinforced with Al2O3 particles. This research has been supported by the National Science Foundation through the grant number HRD 9353547.

INTERNATIONAL SYMPOSIUM ON SULFIDE SMELTING '98: CURRENT AND FUTURE PRACTICES: Session III - Copper Smelting - Converting

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

Program Organizers: Tony Eltringham, BMP Copper, 550 California St., San Francisco, CA 94104-1020; Jussi Asteljoki, Outokumpu Oy, Lansituulentie 7, Espoo Fin-02101 Finland; Pete W.J. Chen, Phelps-Dodge Mining Co., P.O. Box 2860, Silver City, NM 88062; Osamu Ishikawa, Bechtel Corp, Mining & Metals, San Francisco, CA 94119-3965; Robert L. Stephens, Ausmelt Technology Corp., 1331 17th St., Denver, CO 80202; Courtney Young, Montana Tech, Metallurgical Engineering, Butte, MT 59701

Tuesday AM Room: 207
February 17, 1998 Location: Convention Center

Session Chairs: Robert Stephens, Ausmelt Technology Corporation, Denver, CO 80202; Tim Smith, Kilborn SNC-Lavalin Europe, Melrose House, Croydon CR0 2NE United Kingdom

8:30 AM

IMPROVEMENT OF THE CONVERTER'S OPERATION AT TAMANO SMELTER: Tsuneo Maruyama[1]; *Takeo Saito*[1]; Masashi Kato[1]; [1]Tamano Smelter, Hibi Kyodo Smelting Co., Ltd., Okayama-ken 706 Japan

Tamano Smelter of Hibi Kyodo Smelting Co., Ltd. has been operating with one Flash Smelting Furnace with Furnace Electrodes (FSFE) and three Peirce-Smith Converters, two converters hot and one blowing since its start of operation in 1972. Anode production capacity of the smelter has been increased from initial 101,000 to current 263,000 mtpy of copper through the several expansion projects, while the converting process has been improved several times over the years as listed below to increase the converter capacity and to establish stable operations. * Expansion of the converter vessels in length. * Development of automatic scrap charging system of the two kinds for the respective converters, for increase of an instack time and better control of the melt temperature. * Increase of oxygen enrichment in slag and copper blows. * Increase in air flow rate. This paper describes details of the above improvements.

9:00 AM

MODELING SUBMERGED GAS INJECTION OF A PEIRCE-SMITH CONVERTER: *J. Vaarno*[1]; T. Ahokainen[1]; J. Pitkälä[1]; A. Jokilaakso[1]; [1]Helsinki University of Technology, Laboratory of Materials Processing and Powder Metallurgy, HUT FIN-02015 Finland

A commercial CFD-code was used to solve isothermal flow fields of gas and liquid in a Peirce-Smith converter. The model was validated with a 1/4 scale water model and a parametric study. Limits of the modeling technique used were recognized, but calculated results indicate that the present model predicts the general flow field with reasonable accuracy. Therefore, the model was used to examine flow conditions generally and the effect of varying fluid properties and process parameters on the flows. Also, typical scaling factors of physical models were evaluated with the aid of predicted bubble distribution, patterns of the flow field and magnitude of flow velocities. The numerical simulations were found to open new viewpoints to the fluid dynamic related phenomena in the PS-process.

9:30 AM

KENNECOTT - OUTOKUMPU FLASH CONVERTING TECHNOLOGY PURE COPPER BY CLEAN TECHNOLOGY: *Pekka Hanniala*[1]; Ilkka V. Kojo[1]; Markku Kytö[2]; [1]Outokumpu Engineering Contractors Oy, ESPOO FIN 02210 Finland; [2]Outokumpu Technology Oy , ESPOO FIN 02210 Finland

In addition to the fact that the Outokumpu Flash Smelting process is today the most feasible method for matte smelting, the fact that it is also the most environmentally sound method for smelting has been the main decision making criteria in many smelter projects in the past. Thus today over 45% of the world primary copper production is made by utilizing Flash Smelting Technology. It is foreseen that in the near future the global trend will be that all the smelters must decrease their emissions by an accelerating rate, compelling the smelters to make more and more investments on environmental protection. In most of the smelters today, converting is the primary pollution source. The solution today for copper converting and its emissions is the Kennecott-Outokumpu Flash Converting process, which has proven to be the most effective converting method in terms of pollution control and production efficiency including capital and operational costs. The current state of art of the Outokumpu Flash Smelting - Flash Converting process is presented in this paper as well as some totally new options for copper production to be utilized in the near future but which are available already today.

10:00 AM Coffee Break in Exhibit Hall

10:10 AM

SELECTIVE DUST-REMOVAL AT HIGH TEMPERATURE FROM GAS GENERATED DURING A COPPER CONVERTING PROCESS: *Ms. Caisa Samuelsson*[1]; Dr. Bo Björkman[1]; [1]Luleå University of Technology, Div. of Process Metallurgy, 971 87 Luleå Sweden

Experimental studies in laboratory-scale equipment have been conducted to study the vaporization/condensation temperature for metal-compounds in dust generated during the copper converting process. In the present work the vaporization temperature of Zn, Pb, As, Sb and Bi from a dust collected in the electrostatic precipitator after the copper converter are studied. In an earlier study, thermodynamic calculations showed that it is possible to selectively condensate metals at high temperature in a gas atmosphere generated during a copper converting process. The present study was carried out to verify the thermodynamic model. The results indicates that it should be possible for a selective condensation of Zn at high temperature. The temperature required for a selective condensation of Zn depend on the gas atmosphere, e.g., the oxygen potential.

10:40 AM

COMPARISON OF THE OXIDATION BEHAVIOR OF 58% AND 72% COPPER MATTES IN A SIMULATED FLASH CONVERTING FURNACE: *K. M. Riihilahti*[1]; H. Y. Sohn[1]; M. Perez-Tello[1]; A. Jokilaakso[1]; [1]University of Utah, Department of Metallurgical Engineering, Salt Lake City, UT 84112-1183

The oxidation characteristics of solid copper matte particles under simulated Kennecott-Outokumpu Flash Converting conditions are presented. A study was conducted to determine the effects of feed matte grade, matte particle size, temperature, oxygen content of the process gas, solid feed rate and feeding system on the flash converting of copper matte particles. The effects of these variables on overall conversion, degree of sulfur removal, converting quality, fragmentation, particle morphology and mineralogy were determined. The converting quality was highest (-0.77) with the 58% Outokumpu matte at 1100°C. At similar conditions, the 72% Kennecott copper matte was more likely to be unevenly oxidized to produce both sulfur dioxide and copper ox ides and leave unoxidized particle rather than directly produce sulfur dioxide at 1100°C, resulting in an average converting quality of 0.53. The quality of conversion was poorest for the 72 wt-% matte at 920°C (0.35-0.45) at comparable conversion values; the sulfur removal was extremely low even with a relatively high degree of oxidation. Fragmentation of the particles was significant in all cases with the 72% matte. A higher 02/matte ratio and higher temperature, in general, resulted in increased fragmentation while oxygen enrichment had no clear effect. With the 58% matte, particle size was found to increase rather than decrease due to agglomeration and cenosphere formation.

11:10 AM

SURFACE WAVE OF LIQUID BATH BY TOP BLOW GAS JET: Susumu Okabe[1]; Fumito Tanaka[1]; [1]Mitsubishi Materials Corporation, Central Research Institute, Saitama 330 Japan

Top blow injection has been applied to continuous copper smelting and converting by Mitsubishi Materials Corporation since 1974. In this process, injected feeds are captured by and dispersed in the molten bath immediately and effectively, and the reaction is enhanced by the agitation of the bath. The continuous motion of the molten bath, however, may cause severe damage of furnace lining materials, if the injection is not controlled and the furnace is not designed properly. In order to suppress refractory wear, especially at the bath line, the surface wave on the molten bath should be moderated. A cold model study was carried out with a water bath in a cylindrical vessel and the physical model was derived which correlates the oscillation of gas jet impingement on the bath surface and the surface wave. It was found that half of the proper frequency of the gas jet impingement coincides with the proper frequency of the surface wave.

11:40 AM

COPPER CONVERTING AT BINDURA NICKEL CORPORATION USING AUSMELT TECHNOLOGY: *E. N. Mounsey*[1]; B. R. Baldock[1]; [1]Ausmelt Limited, Dandenong, Victoria 3175 Australia

Ausmelt Technology was selected by Bindura Nickel Corporation (BNC) as the basis for a new copper circuit to process nickel plant leach residue to blister, anode and finally cathode copper containing PGM values. The process selected based on Ausmelt Technology to smelt and convert the residue to matte and blister copper and produce a discard slag is novel incorporating three smelting process steps in a single Ausmelt vessel. In addition the process demanded a high quality blister copper product with low levels of arsenic and nickel. This paper reviews the project and the initial operational results to the end of 1997

of the Ausmelt TSL smelt/convert system and discusses the implications for the wider TSL converter market.

INTERNATIONAL SYMPOSIUM ON VALUE ADDITION METALLURGY: Session III - Thin Films and Coatings I

Sponsored by: Extraction & Processing Division, Process Fundamentals Committee

Program Organizers: W.D. Cho, University of Utah, Dept. of Metallurgical Eng., Salt Lake City, UT 84112; H.Y. Sohn, University of Utah, Dept. of Metallurgical Eng., Salt Lake City, UT 84112

Tuesday AM Room: 208
February 17, 1998 Location: Convention Center

Session Chairs: H. Y. Sohn, University of Utah, Dept. of Metallurgical Engineering, Salt Lake City, UT 84112-0114 USA; K. Liddell, Washington State University, Chemical Engineering Department, Pullman, WA 99164 USA

8:30 AM

STRUCTURE AND HYDROGEN-ABSORPTION PROPERTIES OF $LaNi_5$ THIN FILMS PREPARED BY A SPUTTERING METHOD: *Makoto Ohtsuka*[1]; Kentarou Harada[1]; Toru Matsumoto[1]; Kimio Itagaki[1]; [1]Tohoku University, Institute for Advanced Materials Processing, Sendai 980-77 Japan

Thin films of hydrogen storage alloys can be applied for an electrode of rechargeable battery or fuel cell, a filter for H_2 purification and various kind of sensor. It is considered that the difference in the deposition methods or conditions gives a significant effect on their properties. Hence, the structure and hydrogen-absorption properties of $LaNi_5$ thin films were investigated in the present study. $LaNi_5$ thin films were prepared by a sputtering method with a radio-frequency power, W_s, of 50-400W at substrate temperature, T_s, of 323-573K. Nickel content of the films decreased with increasing W_s, however, there was no dependence on T_s. At low W_s and low T_s, morphous films were deposited. In other conditions, the films were polycrystalline. The films prepared at high W_s and low T_s, or at low W_s and high T_s, exhibited only a (h k - O) peak in the X-ray diffraction profiles. This indicates that the c-axis of crystalline films was oriented parallel to the substrate plane. At high W_s and high T_s, the films with columnar structure were obtained. Hydrogen-absorption capacity of the thin films was low compared with the bulk samples. The pressure plateau did not appear on the pressure composition-isotherms. The filters deposited at high T_s represent a higher equilibrium pressure.

8:55 AM

RAPID EPITAXIAL GROWTH OF CONDUCTING AND INSULATING III-V COMPOUNDS ON (001), (110), (111)A, (311)A AND (311)B SURFACES BY HVPE: *S. Lourdudoss*[1]; R. Holz[1]; M. Deschler[2]; R. Beccard[2]; [1]Royal Institute of Technology, Laboratory of Artificial Semiconductor Materials, Department of Electronics, Electrum-229, S-164 40 Kista Sweden; [2]Aixtron Semiconductor Technologies, Aachen D-52072 Germany

Rapid growth of conducting and/or insulating InP, GaAs, $Ga_{O.47}In_{0.53}As$, $GaAs_{O.6}P_{O.4}$ and $Ga_{0.51}In_{0.49}P$ on one or more of (001),(110),(111)A, (311)A and (311)B surfaces by Hydride Vapour Phase Epitaxy (HYPE) is demonstrated. The maximum growth rate of the binaries lies between 12 and 300 μm/hr and of the ternaries between 7 and 170 μm/hr. Room temperature resistivity of insulating InP:Fe and $Ga_{0.51}$ $In_{0.49}P$:Fe can be as high as 5x109 and $lx10_{12}$ ohm cm, respectively. Temperature dependent resistivity and Fe distribution coefficient are analysed. This feasibility of growing insulating layers rapidly on different orientations is very useful for electronic and optoelectronic devices.

9:20 AM

PREPARATION OF HIGH PURITY SILVER THIN FILMS BY LASER MOCVD USING LIQUID SOURCE DELIVERY SYSTEM: *Kiroto Uchida*[1]; Atsushi Itsuki[1]; Sato[1]; Katsumi Ogi[1]; [1]Mitsubishi Materials Corporation, Center Research Institute, Saitama 330 Japan

(BTI4SI3)Ag(hfac) (BTMSE = trans-bis(trimethysilyle)ethene) was chose as a suitable precursor for the XeC1 laser (308nrn) MOCVD of Ag. Iso-propanol solution of (BTMSE)Ag(hfac) was used as a liquid source for the liquid delivery method. High deposition rate 10nm/min at substrate temperatures of 100 and 120°C were obtained at the vaporizer temperature of 100°C. This deposition rate is three times faster than by conventional bubbling method and life of the source and reproducibility of the deposition were also improved. Electric resistivities of the laser deposited film shows significantly low resistivity of 10^{-6} Ωcm compared to 10^{-3} Ωcm of therma1 MOCVD film. These results indicates that the laser MOCVD is one of the effective method for the preparation of the high quality silver film.

9:45 AM

OXYGEN DEFECTS IN METAL OXIDES PREPARED BY LASER CVD FROM METAL ALKOXIDES AND ACETYLACETONATES: *Masakazu Mukaida*[1]; Akio Watanabe[1]; Yoji Imao[1]; [1]National Institute of Materials and Chemical Research, Ibaraki 305 Japan

To clarify the feasibility of alkoxides and acetylacetonates as precursors for laser CVD of metal oxides, vapors of tantalum-, titanium-, and aluminum alkoxide and zirconium acetylacctonate were irradiated by KrF excimer laser and deposits were characterized by XRD and XPS measurements. As for tantalum and titanium, non-stoichiometric crystalline oxides grew nearly phototropically, however, zirconium oxides deposited showed only halo-pattern by XRD measurements. Electric conductivity measurements of tantalum oxides implied the improvement of the insulating properties by the addition of activated oxygen to carrier gas of source materials.

10:10 AM Coffee Break in Exhibit Hall

10:25 AM

DEVELOPMENT OF ROUGHNESS IN ELECTRODEPOSITED MAGNETIC THIN FILMS: *Bo Dou*[1]; KNona Liddell[1]; [1]Washington State University, Chemical Engineering Department, Pullman, WA 99164-2710

In producing multilayer films for magnetic storage applications, the interfacial roughness must be controlled in order to obtain high quality materials with reproducible properties. The present understanding of the effect of roughness on multilayer properties such as magnetoresistance is sketchy, particularly for electrodeposited films. In this study, quantitative atomic force microscopy was used to characterize surface morphology before and after ferro- and paramagnetic films of varying thickness were electrodeposited. The roughness of the film surface was compared with that of the cathude, and the influence of the deposition conditions and film thickness was determined, comparisons were made between Co, Ni and Cu, alloys of these metals, and multilayer films. The thickness of the individual layers was varied between 1 and 50 nm.

10:50 AM

ELECTRODEPOSITION OF CdTe SEMICONDUCTOR FROM AMMONIACAL AQUEOUS SOLUTIONS: *Kuniaki Murase*[1]; Tetsuji Hirato[1]; Yasuhiro Awakura[1]; [1]Kyoto University, Department of Materials Science and Engineering, Kyoto 606-8501 Japan

Polycrystalline CdTe thin film about 1 μm thickness was electrodeposited at 343 K from ammonia alkaline solutions (pH = 10.7) containing TeO_3^{2-} (< 20 mol m^{-3}) and $Cd(NH_3)_4^{2+}$ (60 mol m^{-3})ions. Cathodic polarization curves of the solutions indicate that there is a strong interaction between the two ions; electrodeposition of tellurium is inhibited by the presence of $Cd(NH_{34}{}^{2+}$ ion while that of cadmium is induced by coexistence of TeO_3^{2-}. A formation of precipitate on mixing the dilute solutions of TeO_3^{2-} and $Cd(NH_{34}{}^{2+}$ also suggests the interaction. Increasing $Cd(NH_3)_4^{2+}$ /TeO_3)²mole ratio or decreasing total concentration of ammonia/ammonium-ion gave flat and smooth crystal-

line CdTe deposits at cathode potential -0.7 to -0.3 V vs. SHE. As-deposited CdTe film has a characteristic of n-type semiconductor.

11:15 AM

ELECTRODEPOSITION PROCESS OF Zn-Cr ALLOYS FROM SULFATE BATHS: *Takeshi Ohgai*[1]; Ki Joon-Seo[1]; Tetsuya Akiyama[2]; Hisaaki Fukushima[1]; [1]Kyushu University, Department of Materials, Process Engineering Graduate School of Engineering, Fukuoka 812-81 Japan; [2]Kyushu Sangyo University, Department of Industrial Chemistry Faculty of Engineering, Fukuoka 813 Japan

Abstract Recently, an intensive attention has been paid to the electrodeposition of Zn-Cr in the field of production of super highly corrosion-resistant alloy plated steel sheet of the next generation. In this study the electrodeposition of Zn-Cr alloys from sulfate baths was conducted to investigate the codeposition mechanism of Cr with Zn. As a results, Cr was codeposited with Zn at high current densities in both polyethylene glycol (PEG)-free and PEG-containing baths. However, PEG made it possible to reduce Cr^{3+} to metallic state and Cr existed in the form of Cr^{3+} hydroxide in the deposits obtained from PEG-free bath. The measurements of the partial polarization curve of Zn and the pH in the cathode layer revealed that PEG acted as a polarizer to shift the cathode potential to the reduction potential of the composited hydroxides of Zn and Cr formed due to the pH rise in the cathode layer.

TUESDAY AM

MATERIALS ISSUES IN MICROELECTRONICS: INTERFACIAL REACTIONS, SOLID STATE TRANSFORMATIONS & THERMAL MANAGEMENT: INTERFACIAL REACTIONS AND THERMAL MANAGEMENT-I

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

Program Organizers: Michael R. Notis, Lehigh University, Dept of Materials Science, Bethlehem, PA 18015; Gautam Ghosh, Northwestern University, Dept. of Materials Science, Evanston, IL 60208-3108; Sung Kang, IBM, TJ Watson Research Center, Yorktown Heights, NY 10598

Tuesday AM Room: Centro D
February 17, 1998 Location: Convention Center

Session Chair: Michael R. Notis, Lehigh University, Dept of Materials Science, Bethlehem, PA 18015

8:30 AM INVITED

SOME FUNDAMENTAL MATERIALS ISSUES IN SEMICONDUCTOR PACKAGING: *Dr. Roger J. Stierman*[1]; [1]Texas Instruments, Inc., Dallas, TX 75265-5012 USA

Semiconductor industry roadmaps project that integrated circuit (IC) manufacturers will continue to put more functionality into smaller packages with higher numbers of input/output (I/O) connections. The drive to provide these advanced IC's, along with market forces which keep prices low, put severe process and environmental constraints on the metals and polymers used to make cost-effective packages. At the same time, awareness is growing of the deficiencies in understanding key fundamental materials properties, such as polymer-metal and polymer-polymer interfaces, as well as the lack of knowledge of multiple-element interactions in key ternary and higher order phase diagrams. Some present and future challenges will be presented, along with methods and strategies being used to investigate these critical areas of knowledge.

9:00 AM INVITED

PROCESSING AND PROPERTIES OF CVD DIAMOND FOR THERMAL MANAGEMENT: *Dr. Sungho Jin*[1]; [1]Bell Laboratories, Lucent Technologies, Murray Hill, NJ 07974 USA

One of the many remarkable properties of diamond is its thermal conductivity, about five times that of copper and the highest of all known materials. The high thermal conductivity in combination with the relative ease of diamond film growth by CVD processing makes the material suitable for many applications such as thermal management in high power electronic circuits. For thermal management applications, various processing steps are needed for the diamond films, such as metallization for reliable solder bonding, and metallurgical processes for the planarization of the faceted growth surface and removal of fine-grained diamond regions with poor thermal conductivity. This paper will review the properties and processing of diamond films for thermal management applications.

9:30 AM INVITED

STUDY OF INTERFACIAL REACTIONS BETWEEN TiN AND COPPER: *Dr. Sung K Kang*[1]; Dr. S. Purushothaman[1]; [1]IBM, T. J. Watson Research Center, Yorktown Heights, NY 10598 USA

The interfacial reactions at the solder joints in microelectronics have been extensively investigated in order to control the soldering process and thereby to provide strong and reliable solder joints. The interfacial reactions of interest comprise the dissolution of a base metal into a molten solder, the con- comitant growth of intermetallics in the liquid state, and the growth of intermetallics in the solid state. Various experimental techniques employed include conventional cross-sectional metallography, scanning electron microscopy, electron microprobe analysis, X-ray diffraction and others. In this talk, the inter- facial reaction between tin and copper has been investigated by using differential scanning calorimetry (DSC) which provides a simple means to study such reactions and complements information obtained from other techniques. The experimental results have been applied to understand the interfacial reactions in two important examples: one for a soldering process with copper metallization, and other for a high conductivity, Pb-free, electrically conducting adhesive which contains tin-coated copper powder as conducting filler particles.

10:00 AM Coffee Break in Exhibit Hall

10:15 AM INVITED

PREDICTION OF INTERFACE REACTION PRODUCTS BETWEEN Cu AND VARIOUS SOLDER ALLOYS BY THERMODYNAMIC CALCULATION: *Prof. Hyuck Mo Lee*[1]; Dr. Byeong-Joo Lee[1]; Dr. Nong Moon Hwang[1]; Mr. Seung Wook Yoon[1]; [1]KAIST, Materials Sci. and Tech., Taejon 305-701 Korea

The thermodynamic state at the interface between the substrate and the liquid solder alloys was described by calculating metastable equilibria between the initial phases. It has been shown that the interface composition of liquid could be estimated as the point on the substrate + liquid/liquid metastable phase boundary where the ratios between liquid elements are the same as those in the initial solder alloys. By selecting the phase with the highest driving force under the metastable equilibrium, the intermetallic compound which forms first at the substrate/solder interface could be successfully predicted in agreement with already known experimental information in the case of Cu substrate and Sn-Ag, Sn-Bi, Sn-In, Sn-Pb, Sn-Zn binary eutectic solders. The present scheme can also be applied to the interface reaction of any combination of solid/liquid metals or ceramics if a diffusion and if the phase diagram information on the related systems is available.

10:45 AM INVITED

INTERFACIAL REACTIONS BETWEEN Ni(P) AND Sn-Pb, AND Sn-In SOLDERS: *Dr. Zequn Mei*[1]; Dr. Fay Hua[1]; Dr. Judy Glazer[1]; [1]Hewlett-Packard Co., Electronic Assembly Development Center, Palo Alto, CA 94304 USA

The Cu-Ni-Au layer structure is being extensively used in electronic products as a metal surface for soldering connection, for example, pad on printed circuit board, under bump metallization for flip chip, etc. Because Au dissolves into molten solder, the solderability and therefore the integrity of the solder joint is largely determined by the Ni. Ni is

deposited on Cu either by electrolytic or electroless plating. The electroless plated Ni contained about 10% phosphorus, which causes dewetting during soldering and a weak mechanical interface between solder and Ni. In this work, the interfacial reactions of molten eutectic Sn-Pb and Sn-In with both Cu-electrolytic Ni-Au and Cu-electroless Ni(P)-Au are characterized by wetting balance tests, cross section metallography, and mechanical testing, with emphasis on the effects of phosphorus and indium-containing solder on the kinetics of intermetallic formation, and integrity of the solder joints.

11:15 AM INVITED
INTERFACE MICROSTRUCTURE EVOLUTION OF Sn-Pb,Sn-Bi, AND SN-BI-PB SOLDERS OVER Cu AND ALLOY 42 SURFACES AND ITS EFFECT ON JOINT STRENGTH: *Dr. Fay Hua*[1]; Dr. Judy Glazer[1], [1]Hewlett-Packard Co., Electronic Assembly Development Center, Palo Alto, CA 94304 USA

Alloy 42 (Fe-42%Ni) and Cu are the most commonly used component lead frame materials in the electronics industry. The interfacial intermetallics that form during the soldering process indicate good wetting, but interfacial intermetallics tend to be brittle. The integrity of the solder joint depends on the chemistry, thickness, and morphology of the intermetallics. In this study, the formation and growth of intermetallics during reflow and solid state ageing processes are characterized as functions of temperature and time. The solder alloys are eutectic Sn-Pb, Sn-Bi, and 43Pb-43Sn-14Bi. The effects of the intermetallic chemistry, morphology, and thickness an the solder joint strength are determined by mechanical testing.

11:45 AM
THE EFFECT OF ELECTRIC CURRENT UPON INTERFACIAL REACTIONS: *Dr. Sinn-Wen Chen*[1]; Dr. Wen-chyuarn Liu[1]; Dr. Chih-Ming Chen[1], [1]National Tsing-Hua University, Dept. of Chem. Eng., Hsin-Chu 30043 Taiwan, R.O.C.

Electromigration phenomena have been quite intensively studied recently. mostly in integrated circuit related devices with electric current density higher than 10exp5 A/sq.cm. This study investigated the effect of weaker electric current, up to 10exp3 A/sq.cm., upon the chemically-driven interfacial reactions in the Sn/Cu, Al/Ni and Sn/Ni systems by analyzing their reaction couples, The same intermetallics were formed at the interfaces of the reaction couples either with or without the passing of electric current, such as Cu3Sn and Cu6Sn5 in the Sn/Cu, Al3Ni and Al3Ni2 in the Al/Ni, and Ni3Sn4 in the Sn/Ni couples. The thickness of the reaction layers was about the same for the Sn/Cu and Sn/Ni sysrems. However,dramatic increase of the thickness of the reaction layer in the Al/Ni couples was observed with the passing of electric current, and the degree of enhancement increased with higher electric current density.

MATERIALS PROCESSING FUNDAMENTALS: General

Sponsored by: Extraction & Processing Division, Process Fundamentals Committee

Program Organizers: Patrick R. Taylor, University of Idaho, Dept. of Met & Mining Eng., Moscow, ID 83843-3024; Srinath Viswanathan, Oak Ridge National Lab, PO Box 2008 Bldg. 4508, Oak Ridge, TN 37831-6083

Tuesday AM Room: 206
February 17, 1998 Location: Convention Center

Session Chair: G. P. Martins, Colorado School of Mines, Golden, CO 80401

8:30 AM
OXIDATION BEHAVIOR OF Al3Ti: Xuerong Wen[1]; *Dr. R. G. Reddy*[1]; [1]University of Alabama, Dept of Met & Matls Engrg, Tuscaloosa, AL 35487 USA

The oxidation behavior of Al,Ti intertmetallics have been studied at different times at the temperature of 1000°C in pure dry oxygen. The oxidation rates were investigated using TGA method. The oxidation scales were analyzed using SEM, EDS and X-ray diffraction. The structures of oxides formed at the different oxidation times were observed. The mechanism of oxidation of TiAl3intermetallics were discussed.

8:55 AM
ENHANCED ELECTROCHEMICAL SMELTING REACTIONS BETWEEN IRON OXIDE IN SLAGS AND CARBON IN LIQUID IRON: David E. Woolley[1]; Dr. Harold R. Larson[2]; *U. B. Pal*[3]; [1]MIT, Cambridge, MA 02139 USA; [2]MIT, Room 8-103, Cambridge, MA 02139 USA; [3]MIT, Room 4-049, Cambridge, MA 02139 USA

The rate of reaction between slag containing iron oxide and liquid iron containing carbon is studied. The reaction rate and extent of reaction are related to the oxygen potential in the slag. In blast-furnace-type slags, containing calcia, silica and alumina, with iron as the only mulivalent species, the oxygen potential is related to the activity ratio of ferric to ferrous ions in the slag. The reaction rate is increased by electronically shortcircuiting the slag layer or by applying a voltage across the slag layer (electrolysis). In electrolysis, a plasma arc may be used as the cathode, so that cathodic reactions take place at the plasma-slag interface.

9:20 AM
ELECTROLESS DEPOSITION OF SILVER ONTO ALUMINA SUBSTRATE: J-H. Lee[1]; *G. P. Martins*[2]; [1]Hong Ik University, Dept of Met Engrg & Matls Sci, Seoul 121-791 Korea; [2]Colorado School of Mines, Dept of Met & Matls Engrg, Golden, CO 80401 USA

Silver has the highest electrical conductivity of all metals and consequently this property has been exploited for the conducting devices. Non-conducting substrate such as alumina, when coated with silver offer a means of obtaining desirable electrical properties and at low cost. The research conducted was focused primarily on the development of silver coated alumina balls. The process for coating the alumina balls was based on the use of animoniacal silver nitrate electrolytes containing inhibitor. A formaldehyde solution served as the reductant. The effect of temperature was also investigated. Silver coated alumina ball was assessed by SEM imaging and the adhesion of silver was measured by typical 3M tape test.

9:45 AM
AMPERIOMETRIC SENSOR FOR THE IN-SITU MONITORING OF COMPOSITION AND TRANSPORT PROPERTIES IN HIGH TEMPERATURE METALLURGICAL SLAGS: V. Stancovski[1]; S. C. Britten[2]; *Dr. U. B. Pal*[3]; [1]MIT, Room 4-049, Cambridge, MA 02139 USA; [2]MIT, Room 8-103, Cambridge, MA 02139 USA; [3]MIT, Room 4-134, Cambridge, MA 02139 USA

An in-situ electrochemical technique for measuring the activity, concentration and transport properties of easily dissociable oxides in slags, such as those of iron, chromium, zinc, copper, etc., at temperatures between 1200-1600°C has been developed. The technique utilizes a partically-stabilized-zirconia (PSZ) solid electrolyte to separate a reference-gas compartment from the slag of interest. Three types of measurements, open circuit, amperiometric and electrolytic, are currently under investigation. These measurements yield the desired information on the slag properties.

10:10 AM
MEASUREMENT OF HIGH COPPER CONCENTRATIONS IN MOLTEN SULPHIDE PHASES: A. J. Davidson[1]; *D. J. Fray*[2]; [1]University of Cambridge, Dept of Matls Sci & Met, Cambridge CB2 3QZ United Kingdom; [2]University of Leeds, Dept of Mining & Mineral Engrg, Leeds LS2 9JT United Kingdom

In many copper alloys and matte phases, the concentration of copper is too high for it to be measured by potentiometric solid state sensors, based upon the Nernst equation, as the sensitivity is very low at

high concentrations. In order to overcome this problem, a sensor has been developed where, instead of measuring the potential, a potential is applied and the current measured. Using a cusicon electrolyte, which conducts copper ions, the copper content of alloys and matte phases was measured. It is proposed that this sensor could be used on-line.

10:35 AM

REACTIVE PLASMA SPRAY SYNTHESIS OF TITANIUM CARBIDE: *Dr. Patrick R. Taylor*[1]; Edgar E. Vidal[1]; P. V. Ananthapadmanabhan[2]; [1]University of Idaho, Dept of Met & Min Engrg, Moscow, ID 83844-3024 USA; [2]Bhabha Atomic Research Centre, Laser & Plasma Technology Division, Mumbai 400 085 India

Coatings of TiC/Fe have been produced by Reactive Plasma Spraying using ilmenite ore concentrate as the feedstock powder and methane as the reactive gas. A free energy minimization analysis of the ilmenite-methane system is presented. The coatings have been characterized by x-ray diffraction and SEM. The microstructure of the coatings indicate good interparticle cohesion. The composition of the coating is deficient in iron compared to the initial Fe to Ti ratio found in ilmenite.

11:00 AM

THERMAL DECOMPOSITION OF ILMENITE IN A NON-TRANSFERRED ARC THERMAL PLASMA FLOW REACTOR: *M. Manrique*[1]; Tamara Figueira[1]; Judith Gómez[1]; Patrick R. Taylor[2]; [1]Simón Bolívar University, Dept of Materials Science, Caracas Venezuela; [2]University of Idaho, Dept of Met & Min Engrg, Moscow, ID 83844-3024 USA

The thermal decomposition of ilmenite conentrates in a non-transferred arc thermal plasma flow reactor was investigated. The plasma torch was operated using argon-helium and argon-nitrogen mixtures as plasma gases. The effect of power, feed rate, and particle size was studied. Products were characterized by XRD, SEM, TEM and ICP techniques. Free energy minimization plots were used to predict the thermodynamic behavior of the system under different operating conditions. The results of this investigation showed a significant segregation process where titanium-rich products are collected in the reactor, while iron-rich products are collected in the quenching box and filter. The average size of the product is in the submicron range. Titanium nitride was formed and condensed in the reactor zone when using an argon-nitrogen mixture as the plasma gas.

11:25 AM

PYROHYDROLYSIS: FUNDAMENTALS AND APPLICATIONS FOR THE FERROUS AND NON-FERROUS METALLURGY: *Frank Bärhold*[1]; Albert Lebi[1]; [1]Andritz AG, Ruthner Surface Technologies, Vienna, A-1121 Austria

Pyrohydrolysis is the conversion of metal halides into metal oxides at elevated temperatures. The reaction products are solid metal oxides and a volatile hydrogen halide gas. A lot of metal chlorides and fluorides can be hydrolyzed at temperatures between 250 and 1000ºC. Several alkaline (Na) and Alkaline earth (Ca) metal chlorides as well as some important metal (Pb, Zn) chlorides are not hydrolyzable, since the free enthalpy of reaction is highly positive. By using additives building stable oxides some of the components that will not react in the pure form can be hydrolyzed. The most useful furnaces for this type of high temperature operation are spray roasters, fluid beds and rotary kilns, the latter one of which is of minor importance, since the product is extremely inhomogeneous. The optimum type of reactor mainly depends on the demands on the produced oxide quality. Since many years pyrohydrolysis in spray roast reactors is applied for the total regeneration of hydrochloric acid waste pickle liquors. When pickling mild steel the oxide produced is a highly valuable product that is used in the hard and soft ferrites industry as well as for the production of pigments and ceramics. Extremely high oxide qualities can be reached by removing impurities from the acid in a pretreatment step. For the pickling of stainless steel mixed acid containing hydrofluoric and nitric acid is used. The waste acid contains all components from the pickled steel, mainly chromium and nickel. The metal fluorides can be pyrohydrolyzed like the metal chlorides from mild steel pickling, whereas the nitric acid preferably is evaporated. The aim of this presentation is to show the termodynamical and physical background of pyrohydrolysis and its application in several ferrous and non-ferrous processes.

MICROSTRUCTOLOGY CONNECTING PHASE DIAGRAMS KINETICS & STEREOLOGY TO MICROSTRUCTURAL EVOLUTIONS: F.N. RHINES: Diffusion in Complex Systems

Sponsored by: ASM International: Materials Science Critical Technology Sector, Atomic Transport Committee

Program Organizers: Robert T. DeHoff, University of Florida, Dept. of Materials Sci & Eng., Gainesville, FL 32611-6400; John Morral, University of Connecticut, Dept. of Metallurgy, Storrs, CT 6260

Tuesday AM Room: 103
February 17, 1998 Location: Convention Center

Session Chair: Dan J. Thoma, Los Alamos National Labs., Los Alamos, NM 87545

8:30 AM INVITED

THE VACANCY FIELD AS DETERMINANT OF PARABOLICITY IN MULTICOMPONENT, MULTIPHASE DIFFUSION COUPLE AND/OR OXIDATION RELAXATIONS: *Dr. J S Kirkaldy*[1]; [1]McMaster University, Brockhouse Institute for Materials Research, Hamilton, Ontario L8S 4MI Canada

If D is a characteristic weighted diffusion coefficient for relaxation of the complex interaction zone of an infinite or internally precipitated gas-metal couple then D/X, where X is the mean vacancy atom fraction, represents the order of the mean vacancy diffusion coefficient. With primary metallic species conduction, where mean X of about 1 part in 100 million would be typical, one can conclude that a typical vacancy will cross the reaction zone about 10,000 times for every typical atom crossing implying relative thermodynamic neutrality of the vacancy field. Since X is a nonconserved order parameter we follow convention by invoking the one dimensional time-dependent Ginsburg-Landau equation, containing a conjectured gradient energy analogous to that in type II superconductivity. This is a pseudo-Fick and Schrodinger-like equation with probable solutions wherein for self-consistency, 2M may be taken as approximately equal to D. To complete the analogy the free volume X field acts as the wave function while migrating source-sink dislocations correspond to unpinned normal filaments in type-II near superconductors. Representative practical examples are reviewed. This completes the phenomenological theory of the Kirkendall effect as a special case.

9:00 AM INVITED

INTERDIFFUSION AND PHASE FORMATION IN SELECTED REFRACTORY SILICIDES: *Dr. M. A. Dyananda*[1]; Dr. P. C. Tortorici[2]; [1]Purdue University, School of Materials Engineering, West Lafayette, IN 47907 USA

Multiphase diffusion studies were carried out with refractory metals, such as Mo, W, Re, in contact with MoSi2 at selected temperatures between 900ºC and 1700ºC for the formation of binary and ternary silicide layers. Selected diffusion structures are presented to show the development of both planar and nonplanar morphologies for the individual silicide layers in the multiphase couples. Concepts of integrated and average effective interdiffusion coefficients for the individual components are employed for the description of interdiffusion in the silicides. Examples of uphill diffusion and zero-flux plane development are presented for Mo in ternary (Mo,W)5Si3 and (Mo,Re)5Si3 diffusion layers. New observations of zero-flux planes without the formation of a relative extremum in concentration profiles are reported.

The diffusion structures are discussed in the light of ternary diffusional interactions and the relative diffusion behavior of the diffusing species, and the experimental diffusion paths.

9:30 AM
REACTION BETWEEN SINGLE-CRYSTAL Si AND MONOLYTHIC NBC: *Dr. Y. A. Chang*[1]; Dr. J. Woodford[2]; [1]University of Wisconsin, Department of Materials Science and Engineering, Madison, WI 53705-1595 USA

An examination of the Nb-Si-C phase diagram shows that Si and NbC are not in equilibrium. When Si is brought into contact with NbC at a sufficiently high temperature that the kinetics are favorable, reaction will occur at the interfaces to yield products with a defined microstructure. In this presentation, we will use the principles of thermodynamics/phase equilibria and kinetics of ternary systems to forecast the most likely microstructure formed at constant temperature and pressure. Experimental results will be presented using semi-infinite diffusion couples consisting of single-crystal Si and monolithic NbC. The results obtained are correlated with the forecast microstructure and those obtained using NbC powdered compacts with varying degrees of porosity. This presentation is made to honor Professor F. N. Rhines for his many contributions in the field.

9:50 AM
"PHASE DIAGRAMS IN METALLURGY" AND A MYSTERY ABOUT DIFFUSION PATHS: *Dr. J. E. Morral*[1]; Dr. Caian Qiu[2]; [1]University of Connecticut, Department of Metallurgy and Materials Engineering, Storrs, CT 06269-3136 USA

Rhines was one of the earliest investigators to recognize the connection between microstructures and diffusion paths on phase diagrams. On page 156 of his textbook, "Phase Diagram for Metallurgy," he illustrates this connection with a "schematic representation" that gives the diffusion path on a ternary isotherm as a straight line. Rhines was aware that diffusion paths are not given by straight lines and called this an "erroneous assumption." He also knew that the proper way to draw diffusion paths had not yet been established and called the straight line path" the best approximation that can be made at present." For the past forty years the question of how to properly draw the diffusion path on page 156 has remained a mystery. However recent experimen tal and theoretical work has lead to several answers.

10:10 AM Coffee Break in Exhibit Hall

10:20 AM INVITED
MICROSTRUCTOLOGY OF SOLID STATE REACTIONS: *Dr. Frans van Loo*[1]; Dr. A. A. Kodentsov[1]; [1]Eindhoven University of Technology, Laboratory of Solid State Chemistry and Matrials Science, Eindhoven The Netherlands

The diffusion zone morphology evolved during chemical reaction in an inorganic material system is defined by type, structure, number, shape and topological arrangement of phases. This discussion is confined to the reactive phase formation in a few systems. The first deals with the microstructology of precipitation reactions. Internal nitriding of the Ni-based alloys is considered as an example. The second part of this paper will be devoted to the present understanding of the periodic layer formation during solid state reaction. We distinguish two forms of periodic layered morphology, one consisting of alternating single-phase layers, for example, those occurring in Ag/Ti foil/Si "sandwich" diffusion couples. This can be described as a Liesegang phenomenon. The other, a periodic array of two phase bands in single phase matrix occurs, for example, in Ni/SiC, Pt/SiC systems. The periodic layers consist of interwoven bands of particles. Periodicity results from a repeated "splitting" of the interwoven band as a result of the Kirkendall effect.

10:50 AM INVITED
NITRIDATION OF TITANIUM ALLOYS - THERMODYNAMIC ASPECTS: *Dr. Rainer Schmid-Fetzer*[1]; [1]University Clausthal, Electronic Materials, Clausthal-Zellerfeld Germany

The nitridation of Ti alloys and the interactions of TiN with metallic elements form the basis of important applications in materials processing. A thermodynamic approach is presented to analyze these processes and the formation of phases in relation to the stable and metastable ternary Ti-Al-N and Ti-Ni-N phase equilibria. The following examples are discussed: (1) Denitrification, phase formation, and vaporization during cermet sintering of TiN-Ni mixed powder compacts. Ranges of preferred metal vaporization during vacuum processing are also given. (2) Reactions during in-situ processing of GAMMA-TiAl-"Ti2AlN" composites are quantitatively explained. This includes even the peak temperatures observed during the combustion process. (3) Mixed coatings of TiAl3+TiN on titanium are useful to improve both the oxidation resistance (with TiAl3) and the hardness (with TiN). Two different processing routes were studied, nitridation after aluminization and vice versa. Distinctly different microstructures are obtained in the graded layers.

11:20 AM
DIFFUSION ON POLYSYNTHETICALLY-TWINNED INTERFACES IN TiAl: *Prof. David E. Luzzi*[1]; Mr. Dai Imamura[2]; Prof. Haruyuki Inui[2]; Mr. Masahiro Kawasaki[3]; Mr. Hidehiro Yasuda[4]; Prof. Hirotaro Mori[4]; Prof. Masaharu Yamaguchi[2]; [1]Univ. of Pennsylvania, Materials Science and Engineering, Philadelphia, PA 19104-6272 USA; [2]Kyoto University, Materials Science, Sakyo-ku, Kyoto 606-01 Japan; [3]JEOL, Ltd., Akishima, Tokyo Japan; [4]Osaka University, Res. Center for UHVEM, Suita, Osaka Japan

Polysynthetically-twinned (PST) TiAl, containing a high density of parallel, atomically-flat interfaces of identical crystallographic orientation, is an excellent model system for a detailed investigation of interface diffusion. Macroscopic PST crystals were grown in an optical float zone furnace. Thin films were cut from oriented crystals and polished with <110> and <112> directions normal to the film. After sputter cleaning, either Ag or W was deposited on one side of the TiAl thin films. The atomic transport of the Ag and W through the films along the interfaces was measured using in-situ heating experiments in an Auger microprobe, the well-known Hwang-Balluffi accumulation experiment. The Auger results were correlated with high-resolution structural and chemical analyses of the interfaces using transmission electron microscopy. The goals of these experiments are to make the first absolute determination of an interface diffusion coefficient by using the TEM to characterize the interface width, and to study the influence of interface crystallography on interface diffusion.

11:40 AM
JUMP FREQUENCY MODELS FOR DIFFUSION SIMULATION IN MULTICOMPONENT SYSTEMS: Dr. Coimbatore V Iswaran[1]; Dr. Robert T DeHoff[3]; *Mr. Nagraj Kulkarni*[1]; [3]University of Florida, Department of Materials Science and Engineering, Gainesville, Florida 32611 United States

A simple meaningful description of intrinsic diffusion based on "effective jump frequencies" has the potential of simulating diffusion in multicomponent systems with minimal experimental effort. The success of this procedure is dependent on the development of appropriate jump frequency models for the particular system under study. Previously the development of these models was based on a semi-quantitative "informed trial and error procedure" that involved analysis of interdiffusion data for a few select diffusion couples in a given system. An alternate procedure is presented by which the jump frequency models may be directly determined from intrinsic diffusion data. The possibility of building multicomponent jump frequency models from those based on the binary segments is explored. A demonstration of the simulation package, written in MathCad Plus, will be given at the end of the session.

MICROSTRUCTURE AND ITS EFFECTS ON AMORPHOUS NANOPHASE & NANOCRYSTALLINE MATERIALS: Session III - Interface and Grain Growth

Sponsored by: ASM International: Materials Science Critical Technology Sector, Flow & Fracture Committee, Jt. Electronic, Magnetic & Photonic Materials Division/Structural Materials Division, Alloy Phases Committee, Chemistry & Physics of Materials Committee, Structural Materials Division, Physical Metallurgical Committee

Program Organizers: Ram B. Bhagat, Pennsylvania State University, 227 Hammond, University Park, PA 16802; Robert D. Shull, NIST, Bldg. 223 Rm. B152, Gaithersburg, MD 20899; Stephen Spooner, Oak Ridge National Lab, Solid State Division, Oak Ridge, TN 37831

Tuesday AM Room: 205
February 17, 1998 Location: Convention Center

Session Chairs: Stephen Spooner, Oak Ridge National Laboratory, Solid State Division, Oak Ridge , TN USA; J. Eckert , Institut fur Festkorper-und Werkstofforchung Dresden, Institue fur Metallische Werkstoffe, Dresden D-01171 Germany

8:30 AM Opening Remarks

8:40 AM INVITED
INTERFACES STRUCTURE ROLE ON THE MAGNETIC AND MECHANICAL BEHAVIOUR OF NANOCRYSTALLINE IRON: *E. Bonetti*[1]; L. Del Bianco[1]; [1]University of Bologna, Dept.of Physics and Istituto Nazionale per la Fisica della Materia, Bologna I-40126 Italy

The understanding of the structure of interfaces is one of the up to date open and controversial issue in the investigation of 3D nanostructured materials. From a general point of view it seems now quite firmly established that the structure and properties of interfaces in nanocrystalline materials strongly depend on how the material is prepared as for example by using high equilibrium or non equilibrium techniques. Recently both theoretical and experimental investigations have indicated that a two phase model (grains and interfaces) seems appropriate to account for some observed behaviour of the thermodynamic and transport properties of bulk nanophase materials. The study of how the structure of the interfaces may give rise to strongly different physical be haviour was adressed by employing different techniques: mechanical spectroscopy, Mossbauer spectroscopy, XRD, EXAFS on nanocrystalline iron prepared by mechanical attrition under strictly controlled conditions up to an ultimate grain size of 8-10 nm. The re sults show that significant modifications of the measured quantities are induced by thermal relaxation of the structure without appreciable grain growth. In particular a worth relationship between the structural configuration, the mechanical behaviour in the anelastic regime and the magnetic behaviour was established. Possible phase transitions and impurity effects involving the interfaces are discussed to account for the observed behaviour.

9:20 AM
STABILITY OF A NANOCRYSTALLINE STRUCTURE IN TiAl-BASED ALLOYS: *Dr. Oleg N. Senkov*[1]; M. L. Övecoglu[2]; N. Srisukhumbowornchait[1]; F. H. Froes[1]; [1]University of Idaho, Institute for Materials and Advanced Processes (IMAP), Moscow, Idaho 83844-3026; [2]Istanbul Technical University, Istanbul 80626 TURKEY

Two fully dense nanocrystalline TiAl-based compacts, i.e. Ti-47.5Al-3Cr and Ti-48Al-2Nb-2Cr, were synthesized by hot isostatic pressing (HIP'ing) from mechanically alloyed powders. Microstructure evolution and phase transformations during mechanical alloying, HIP'ing, and heating were studied with the use of TEM, SEM, XRD and DTA. Formation of amorphous phases was detected in both powders after 15 hour mechanical alloying. During HIP'ing, crystallization of the amorphous phases occurred and very fine equiaxed gamma-TiAl grains were formed. The grain size decreased when the temperature of HIP 'ing was decreased, and it was 42 nm after HIP'ing at 725°C. Grain growth occurred during annealing of the HIP'd alloys, which could be described by a single thermally activated process limited by a permanent pinning force. The activation energy of the grain growth was close to the activation energy for lattice diffusion of Ti in TiAl. Microhardness decreased with the annealing time and followed to the Hall-Petch depe ndence on the grain size.

9:40 AM
INFLUENCE OF INTERFACIAL STRUCTURES ON THE MELTING OF Pb NANOCRYSTALS EMBEDDED IN Al MATRICES: *H. W. Sheng*[1]; K. Lu[2]; Dr. En (Evan) Ma[1]; [1]Louisiana State University, Department of Mechanical Engineering, Baton Rouge, LA 70803 USA; [2]Chinese Academy of Science, Institute of Metal Research, Shenyang 110015 China

Size-controllable Pb nanocrystals were homogeneously embedded in Al matrices via ball-milling and melt-spinning techniques. The interfacial structure varied with the processing route: for ball-milled dispersions, the embedded Pb nanocrystals were randomly oriented with incoherent interfaces with the Al matrix; while in the melt-spun samples, the nanocrystals were epitaxially oriented with the Al matrix. The melting behavior of these embedded nanoparticles has been studied using differential scanning calorimetry in combination with in situ X-ray diffraction (XRD) analyses. It was found that the melting point of the nanocrystals with incoherent interfaces was depressed, whereas the nanocrystals with epitaxial interfaces could be appreciably superheated. In both cases, the deviation of the melting point from that of bulk Pb was proportional to the reciprocal nanocrystallite size. The influence of interface was further correlated with changes in Debye temperature. Using quantitative XRD analyses, the Debye temperatures of the epitaxially oriented Pb particles (11 nm) and incoherently oriented Pb particles (19 nm) were determined to be 98 K and 69 K, respectively. This contrasting behavior in Debye temperature deviation away from the bulk value (84 K) is attributed to the different nature of the interfacial structures and presumably responsible for the different melting behavior of the embedded Pb nanoparticles according to the Lindemann's melting criteria.

10:00 AM
GRAIN GROWTH IN NANOCRYSTALLINE Pd-Zr ALLOY: A SOLUTE DRAG APPROACH: *Dr Zi-Kui Liu*[1], [1]University of Wisconsin-Madison, Materials Science and Engineering, Madison, WI 53706 USA

One of the most important issues in nanocrystalline materials is to understand and control the growth of nanometer-sized grains. The primary driving force for grain growth is the excess energy associated with grain boundaries. Therefore, a reduction in grain boundary energy would result in a decrease in driving force for grain growth. This may be realized to some extent by introducing a foreign component which tends to segregate to the grain boundaries. On the other hand, grain growth can be hindered by increasing the dissipation of driving force needed to move the interface. In our recent work on interfacial kinetics, the effects of interfacial mobility, interfacial solute drag and interfacial curvature on interface migration were discussed in a consistent framework. It was found that the segregation of one component to the interface can reduce the interface migration rate by orders of magnitude. In present work, we will investigate the interfacial migration in Pd-Zr alloy at different Zr content by using our solute drag model and the thermodynamic property of the alloy in literature, and compare the calculations with available experiment information. It will be shown that, when Zr content is above a critical value, the excess amount of Zr segregated to the interface will prevent the grain boundary migration due to the interfacial solute drag effect. This phenomenon can contribute to understanding and designing nanocrystalline alloys.

10:20 AM

CRYSTALS AND NANOCRYSTALS IN RAPIDLY SOLIDIFIED Al-Sm ALLOYS: *P. Rizzi*[1]; C. Antonione [2]; M. Baricco[1]; L. Battezati[1]; L. Armelao[3]; E. Tondello[3]; M. Fabrizio[4]; S. Daolio[4]; [1]Universita di Torino, Dipartimento di Chimica IFM, Torino Italy; [2]Politecnico di Torino, Dipartimento di Ingegneria Chimica e Scienza dei Materiali, Torino Italy; [3]Universita di Padova, Dipartimento di Chimica Inorganica, Metallorganica ed Analitica, Padova Italy; [4]Istituto di Polarografia ed Elettrochimica preparative, CNR, Padova

The formation, size and morphology of crystals in Al_{100-x} Sm_x ($8 < x < 14$) alloys either melt spun or crystallized from the glass was analyzed with a combination of techniques (SEM, AFM, TEM, DSC, XPS, SIMS). AFM and SEM show localized crystalline fractions even in ribbons appearing amorphous at XRD. On the dull surface colonies of crystals were often found, apparently nucleated on heterogeneities. In Al_{92} Sm_8 globular crystals were identified by TEM as a-Al, with size of 500 nm, in the ridges caused by the wheel surface. In Al_{88} Sm_{12}, dendritic crystals were identified as Al_{11} Sm_3 by XRD. On the shiny side of Al_{92} Sm_8 ribbons, AFM reveals globular crystals, 100-200 nm in size, regularly distributed and hardly detected by SEM. They were very likely nucleated in the undercooling regime. In glass samples annealed between 155°C and 171°C TEM shows globular nanocrystals reaching a density of 1022 m^{-3} in less than a minute with maximum size of 20 nm. In Al_{90} Sm_{10}, ribbons crystals seen with AFM have sizes around 10 nm. SEM shows larger particles having contrast and shape as Al_{11},Sm_3 in Al_{88} Sm_{12}. The bulk crystallization occurs via a polymorphic reaction. The variety of crystallization processes is discussed by evaluating their driving forces as a function of temperature and composition and establishing a hierarchy in phase stability.

10:40 AM INVITED

SINTERING OF SILVER AND COPPER NANOPARTICLES ON (001) COPPER OBSERVED BY IN-SITU UHV TEM: *M. Yeadon, PhD*[1]; R. S. Averback[1]; J. W. Bullard[1]; J. M. Gibson[1]; [1]University of Illinois at Urbana-Champaign, Materials Research Laboratory, Urbana, IL 61801 USA

The sintering of copper and silver nanoparticles with single crystal substrates of both copper and silver has been studied using a novel UHV in-situ TEM. The system is equipped with a UHV DC sputtering attachment enabling metal nanoparticles to be generated and transfered directly into the microscope in the gas phase. In the case of copper particles on (001) copper, the particles are initially randomly oriented on the substrate. Upon annealing, however, the particles reorient and assume an epitaxial orientation with the substrate. The process apparently occurs by a mechanism involving sintering and grain growth. In the case of silver on copper, grain growth cannot occur since the metals are immiscible. Our observations show that the particles wet the substrate surface and form a thin epitaxial film with the orientation relationship (lll)Ag // (001)Cu, [110]Ag // [110]Cu. The experiments have been performed in parallel with molecular dynamics simulations of particle: substrate interactions. We present our observations and discuss the results of preliminary investigations of the sintering of other particle: substrate combinations.

11:20 AM

A MOLECULAR DYNAMICS STUDY ON THE LIQUID-AMORPHOUS-CRYSTALLINE TRANSITION IN NANOCRYSTALLINE PLATES: *H. K. Chang*[1]; B. K. Cheong[2]; W. M. Kim[2]; M. Chung[2]; T. S. Lee[2]; S. G. Kim[2]; J. K. Lee[3]; [1]Sung Kyun Kwan Univ., Dept. of Metallurgical Eng., Suwon Korea; [2]KIST, Seoul Korea; [3]Michigan Tech. University, Dept. Metallurgical Eng., Houghton, MI 49931 USA

As an emerging mass-data storage technology, phase change optical recording makes use of the difference in reflected light intensity between the amorphous and crystalline state of chalcogenide nanocrystalline plates. For a better understanding of the transition behavior in such thin plates, a constant-pressure molecular dynamics study is performed for Lennard-Jonesian fcc plates. The melting point depression is found to range from 3% for a plate with 60 atomic layers up to 75% for a two-atomic layer plate. A plate with a (111) orientation shows a depression slightly less than that of a (100) plate. Phase transitions begin at a free surface and advance inward. Consequently, the critical quench rate (CQR) for amorphization displays a higher value for a plate than for a bulk state. For a binary alloy, the CQR decreases with an increase in size difference between solvent and solute atoms, and with an increase in the solute concentration. The onset of crystallization from an amorphous phase displays a lower temperature for a plate than that for a bulk state.

11:40 AM

NANOSTRUCTURED ALLOYS OF Fe-xAl FORMED BY MECHANICAL PROCESSING: *Desmond C. Cook*[1]; Rama Balasubramanian[1]; J. C. RAWERS[2]; [1]Old Dominion University, Physics Department, Norfolk, VA 23529 USA; [2]Albany Research Center, U.S. Department of Energy, Albany, OR 97321

Alloys of Fe-xAl (where x = 0-20 wt.%) were produced by mechanically processing blended iron and aluminium powders in argon gas for times of 25, 50, 100 and 150 hours using an Attritor ball-mill. The effect of mechanical alloying on some of the nanocrystalline and microstructural properties as a function of different processing times was investigated using Mössbauer spectroscopy and X-ray diffraction. In processing the samples in an inert gas environment, a continuous decrease in the grain size was observed for aluminium concentrations up to 5 wt.%. However, for aluminium concentration above 8 wt.%, the grain size decreased quickly, for processing times less than 50 hours and then remained constant. The Mössbauer analysis indicated that after 50 hours of processing, the aluminium was not uniformly distributed in the iron lattice. However after 100 hours of processing, the aluminium was uniformly distributed and its site occupancies followed closely those predicted by the binomial distribution for substitutional aluminium randomly distributed in a b.c.c. lattice. The X-ray analysis showed that for aluminium concentrations greater than 2 wt.%, after 50 hours of processing, nearly 95% of the aluminium had been incorporated into the iron lattice, and that 100% was incorporated after 100 hours of processing. For a processing time of 150 hours, the lattice parameter increased continuously as a function of aluminium concentration up to and including 10 wt.%. However, the lattice parameter remained constant at 0.2900 nm for greater aluminium concentrations up to 20 wt.%. A detailed analysis of the effect of mechanical alloying on the microstructural properties of the Fe-xAl system will be presented.

MODELING THE MECHANICAL RESPONSE OF STRUCTURAL MATERIALS: Session I: Numerical Simulations

Sponsored by: Structural Materials Division, Structural Materials Committee

Program Organizers: Eric M. Taleff, The University of Texas, ASE/EM CO600, Austin, TX 78712; Rao Mahidhara, Cypress Semiconductor Corp, San Jose, CA 95134

Tuesday AM Room: 202
February 17, 1998 Location: Convention Center

Session Chairs: R. D. Wood, University of Wales Swansea, Department of Civil Engineering, Swansea, Wales SA2 SPP UK; A. B. Geltmacher, FM Technologies, Fairfax, VA 22032

8:30 AM INVITED

NUMERICAL SIMULATION OF SUPERPLASTIC FORMING: *R. D. Wood*[1]; J. Bonet[1]; [1]University of Wales Swansea, Department of Civil Engineering, Swansea, Wales SA2 SPP U.K.

The numerical simulation of superplastic forming with diffusion bonding using the finite element method has been available to industry for a numbor of years. However it remains the case that practitioners in the field, that is, those who make the products, generally remain sceptical of the possibilities afforded by the method. This is due to a number of factors; (a) the finite element formulations are mathemati-

cally complex, (b) the software cannot be operated independently of some knowledge of the numerical process and, (c) a general level of ignorance of the finite element method as applied to such complex metal forming processes as superplastic forming leads to an over optimistic expectation of the software and a resulting disappointment in its performance. This paper will briefly overview the finite element formulation of superplastic forming particularly from the perspective of the above remarks. A number of examples will be given to demonstrate the potential of the method. Finally some comments will be made relating to technology transfer between academia and industry. This latter topic is particularly important since it is the author's experience that the potential benefit of such software can only be realised if industry puts in place management structures and training procedures that involve a continuum of expertise from numerical analysts to component and manufacturing process designers. The review paper cited below [1] together with a paper on virtual manufacturing [2] provide the reader with a comprehensive set of references to the topic. Wood, R.D. and Bonet, J., A review of the numerical analysis of superplastic forming, Jnl. of Materials Processing Technology, 60, 1996, pp. 45-53. Wood, R.D. and Bonet, J., Superplastic forming simulation - A case study for virtual manufacturing, Proc. of Conf. on Virtual Manufacturing, The Royal Aeronautical Society, London, 1996, pp. 7.1-7.7, ISBN 1 85768 013

9:00 AM

FINITE ELEMENT MODELING OF SUPERPLASTIC FORMING OF TITANIUM HELMET ARTICLES: *S. M. El-Soudani*[1]; M. Jamjian[2]; J. Mackiewicz[3]; K. Newell[4]; [1]Boeing Defense and Space Group, North American Aircraft Division, Seal Beach, CA 90740-7644 ESI North America; [2]Engineering Systems International, San Diego, CA ESI North America; [3]U. S. Army Research Laboratory, Natick, MA ESI North America; [4]Rockwell International Corporation, Thousand Oakes, CA ESI North America

Superplastic forming (SPF) of single-sheet, and diffusion-bonded multi-sheet structures has been in use for some time in certain military and commercial, light-weight structural applications. Ample opportunities for industrial usage of this process so far have been limited to the aerospace and automotive fields. Ballistic-resistant army and Law-enforcement personnel helmets impose even more stringent demands of light-weight and high-performance structural integrity compared to other military and aerostructures applications. Despite the initial progress in the aircraft and automotive SPF usage, a serious challenge to the application of the SPF process remains to be the final product thickness uniformity, particularly in situations involving high depth-to-width ratios of the final superplastically formed (or deep drawn) products. Helmet shell fabrication by this method challenges the limits of superplastic forming of single-sheet shell structures, as it often requires surface-to-projected-area ratio in the r ange of 2.5 to 3, thus exceeding that of a hemisphere. Prior attempts to superplastically form hemispherical pressure vessel halves revealed a natural trend of final formed part thickness tapering down to a minimum in the dome area by nearly a factor of 2 to 3. Trial-and-error methods for dealing with the problem may prove costly and time-consuming, if their goal is to reduce, or completely eliminate the trend for natural thickness taper, as well as the SPF inherent localized thinning, which in turn could be further superimposed on the natural taper from the use of inadequate parameters of the microstructure and/or strain rate sensitivity of the flow stress (so-called m-value). Using a modified explicit finite element code originally developed by the ESI Group in Paris, for commercial metal-stamping simulation known as PAM-STAMP, an attempt is made in this paper to simulate the helmet SPF process, whereby the interplay of various material forming characteristics, initial preform design, and processing parameters (temperatures, forming gas pressure-time schedules, etc.) can be subject to experimentation and process design with a computer. Preliminary trial runs have been completed, whereby the results of a measured degree of success, and the needs for further refinement of SPF process modelling are discussed. Successful implementation of this technology could benefit areas other than ballistic-resistant helmet fabrication, such as a multitude of compound curved aerodynamic titanium and aluminum shell structures, domes, nose cones, fuel tanks, pressure vessels, etc.

9:20 AM

THE EFFECT OF FORMING IN THE DESIGN OF DEEP-DRAWN STRUCTURAL PARTS: *Dr. Guy C. M. Marron*[1]; P. F. R. Patou[1]; [1]Sollac groupe Usinor, CRPC - DB26, Cedex, France

During the forming process of sheet steel, numerous secondary physical phenomena occur and accompany the change of shape. The most obvious effect is the thickness variation which induces some variations in in-service stresses. However other effects also take place, such as residual stress, strain hardening and damage. Young's modulus variation etc. All these effects have an influence on admissible stress and rigidity. Traditionally, the designer does not take into account these effects, which are considered as being negligible. Not even the thickness variations - which can reach approximately 20% are considered. The aim of this paper is to classify these secondary effects according to their influence on the behavior of the part in service on its fatigue life and therefore on weight saving. For this purpose, the results of numerical stamping simulation are introduced in an analytical model coupled to an FEM analysis code. The fatigue criterion used in this demonstration is that of Dang Van. The risk of fatigue failure can be estimated with accuracy using this approach, which takes into consideration the actual mechanical properties of the material, at any point in the part. An example of application in the automotive industry is detailed. It shows how profitable this approach can be towards weight reduction. This approach can also be useful in other domains, such as crash resistance. It is necessary to take into account these secondary effects which occur during metal forming, in order to optimize the use of the steel. The result is safety improvement, increased fatigue life, improved crash resistance, and also weight and cost reduction.

9:40 AM Coffee Break in Exhibit Hall

9:50 AM

UNBIASED COMPUTATIONAL TECHNIQUES USED TO MODEL ASYMMETRIC LOCALIZATION IN TENSILE SPECIMENS FOR MATERIAL CHARACTERIZATION: *Dr. Andrew B. Geltmacher*[1]; P. Matic[2]; R. K. Everett[2]; [1]FM Technologies, Inc, Fairfax, VA 22032 USA; [2]Naval Research Laboratory, Mechanics of Materials Branch, Code 6382, SW, Washington, DC 20375 USA

The present study develops a constitutive parameter characterization methodology that produces accurate material parameters from both experimental and finite element analyses. This methodology utilizes an ABAQUS finite element model of the experimental test specimen to reproduce the experimentally determined load-displacement and specimen shape evolution. A number of techniques are examined to use the observed neck asymmetry as an additional measure of solution sensitivity. The techniques are selected to reproduce localization asymmetry without previously biasing the necking location in the model of the tensile specimen. The computer simulation with the accurate constitutive parameters reproduces the deformation evolution and necking asymmetry from the experimental tests for such diverse materials as HY100 steel and b21S titanium.

10:10 AM

FINITE ELEMENT MODELLING OF THE FORMATION OF DISLOCATION CELL STRUCTURES: *H. Feng*[1]; M. Nabil Bassim[1]; [1]University of Manitoba, Metallurgical Sciences Laboratories, Department of Mechanical and Industrial Engineering, Winnipeg, Manitoba R3T 5V6 Canada

Theories of work hardening have been based on the occurrence of dislocation cell structures whose size is related to the applied stresses. This present study further examines the occurrence of these structures using a finite element (FE) modelling approach to simulate the formation of dislocation cell structures during tensile deformation. The FE-model considers deformation of several grains. In each grain different anisotropic elastic module and plastic yield strengths are examined. Fluctuations of the yeild strengths and the different favorable slip directions in each grain are taken into account. This dislocation cell structure was studied by simulating the local residual internal and related elastic strains in each grain. Their magnitude and distribution are usually related to dislocations introduced by plastic deformation. Therefore, the dislocation distribution is indirectly reflected by the distributions of residual stresses and elastic strains after unloading. The calcu-

lated results indicate that, after plastic deformation of tensile experiments, there are non-uniform residual stresses and strains in the grains with different anisotropic yield stresses and different favorable slip directions. Such residual stresses appear in a form similar to that of dislocation cell structures. The more the fluctuation of the local yield strength and of the local favorable slip direction in a grain are, the more significant the dislocation cell structure becomes. In the case where there is no fluctuation, the dislocaiton cell structure does not occur. Hence, it was concluded that the formation of dislocation cell structures in metals are influenced by the fluctuation of the local anisotropic yeild strengths andof the local favorable slip directions in each grain.

10:30 AM

MODELING THE MECHANICAL RESPONSE OF AN W/NB-1ZR COMPOSITE SYSTEM.: *Dr. Louis J. Ghosn*[1]; Dr. Sai V. Raj[1]; [1]NASA Lewis Research Center, Structures Division, Cleveland, OH 44135 U.S.A

Due to the expected demand for high power requirements for future space explorations, NASA envisions building the future generation space crafts powered by nuclear reactors, using molten lithium as the reactor coolant. The candidate material for the fuel clad tubes with demonstrated compatibility with molten lithium, that met the stringent design creep lives, is a Nb-1(wt.%)Zr matrix alloy reinforced by continuous 218 tungsten (W) wires (henceforth, called W/Nb-1Zr composite system). Before building such a power system, the mechanical behavior of W/Nb-1Zr system has to be established for the designers. This presentation demonstrates the strategies used to model the mechanical behavior of the W/Nb-1Zr composite system. The finite element method was used to determine the mechanical behavior of various fiber volume fractions of the W/Nb-1Zr system (20 to 70%) at various temperatures (1400 to 1600K) and various strain rates (1.6x10-5 to 1.6x10-3 sec-1). Axisymmetric meshes of concentric cylinders containing a single fiber encased by a cylindrical matrix were generated. Elastic-plastic rate dependent constituent material properties were used in the present analysis. The processing history was included to better ascertain the residual stresses and plastic strains of the constituents due to the mechanical properties mismatch between the W fiber and the Nb-1Zr matrix.

10:50 AM

EFFECTS OF TiN INCLUSIONS ON STRESS AND STRAIN DISTRIBUTION OF AN ULTRA HIGH STRENGTH STEEL: *Ms. Jinhong Yang*[1]; [1]Oregon Graduate Institute of Science and Technology, Materials Science, Portland, OR 97229 USA

Engineering metallic materials usually contain various microscopic inclusions and the inclusion shape may be controlled by the solidification and thermal-mechanical processing. Finite element method and ANSYS program was used for studying the effects of TiN inclusions on the stress and strain aggregation behavior in an ultra high strength steel. Different shapes and inclining angles to the tensile axis were considered. It was found that triangle TiN is more dangerous than square and hexagon TiN. The relationship between peak equivalent stress and inclining angles is in a wave form. Lots of research has been done for microvoid nucleation by the inclusion interface debonding. However, microvoids also can be formed when inclusions crack. In this study, the tensile strength of TiN Whiskers was taken as the critical stress for a crack to initiate inside a TiN inclusion. The corresponding strain in the matrix calculated by ANSYS program is compared with the true strain measured by strain gauge.

11:10 AM

SIMULATING DUCTILE FRACTURE OF HY-100 STEEL AT DYNAMIC STRAIN-RATES BY CRYOGENIC, QUASI-STATIC STRAIN-RATE TESTS: *V. Jablokov*[1]; [1]Penn State University, Dept. Mat'ls. Science & Engr., University Park, PA 16802

Under service-related loading conditions, structural steels such as HY-100 may fail at high loading rates and under multiaxial stress states. This study examines the simulation of dynamic failure at room temperature by quasi-static tests at cryogenic temperatures. Using the thermal-activation based Mechanical Threshold Stress constitutive flow model to predict the cryogenic test conditions, we have tested circumferentially notched tensile specimens of HY-100 steel at 10^2/s and room temperature as well as at -85C and either a 1/s or 10^{-3}/s strain rate. The failure strains, damage evolution, and the failure mechanisms have been determined from the above conditions and as a function of imposed stress triaxiality. In particular, the failure behavior under the cryogenic/quasi-static conditions is contrasted to that observed at room temperature at the dynamic strain rate. This work is supported by the Office of Naval Research, Naval Surface Warfare Center, and the Los Alamos National Laboratory.

11:30 AM

EFFECT OF THRESHOLD STRESS PROCESSES ON CREEP BEHAVIOR: *F. A. Mohamed*[1]; [1]University of California, Dept. Chemical and Biochemical Engrg. and Materials Science, Irvine, CA 92697 USA

The operation of a threshold stress process signifies that the mechanical deformation of the material is not driven by the total applied stress, but rather by an effective stress. By incorporating a threshold stress for creep, which depends strongly on temperature, in basic deformation processes proposed for metals and simple alloys, it is demonstrated that the creep behavior of several types of materials can be predicted. Examples for these types of materials include powder metallurgy Al alloys, discontinuous Al matrix composites, and superplastic alloys.

NON-AEROSPACE APPLICATIONS OF TITANIUM & ITS ALLOYS: Session III - Heat Exchanger, Chemical Process Applications

Sponsored by: Structural Materials Division, Titanium Committee
Program Organizers: F.H. (Sam) Froes, University of Idaho, IMAP-Mines Bldg. #321, Moscow, ID 83844-3026; P.G. Allen, Timet, P.O. Box 2128, Henderson, NV 89009; M. Niiomi, Toyohashi Univ of Technology, Dept. of Production Systems Eng., Toyohashi 441 Japan

Tuesday AM Room: 101
February 17, 1998 Location: Convention Center

Session Chair: J. S. Grauman, TIMET, Henderson Technical Laboratory, Henderson, NV 89015

8:30 AM

RESISTA-CLAD PLATE: CLAD PLATE TECHNOLOGY FOR DUCTWORK, CHIMNEY LINERS AND ABSORBERS IN FLUE GAS DESULFURIZATION UNITS: *Mr. Mark A. Phillips*[1]; [1]SPF Corporation of America, Midlothian, VA 23113

Resista-Clad Plate offers a reliable, cost effective solution to severe corrosion problems encountered in wet Flue Gas Desulfurization systems for either new or retrofit construction. Resista-Clad Plate uses a patented technology to weld-bond thin gauge (.50mm to 2.0mm) corrosion resistant materials such as titanium to relatively thick (1.6mm to 76mm), significantly less expensive carbon steel. Titanium Resista-Clad Plate and Titanium Overlap Panels, produced by the Resista-Clad Plate Process, have been extensively used in FGD systems since 1984 with over 550,000 s.f. used in outlet ductwork, chimney liners and absorbers. In addition this technology has been used and proven successful in hundreds of demanding applications in the chemical process industry (that in general have more severe corrosive environments under full vacuum, than FGD applications) since the development of the process in 1975. This paper presents and discusses the Resista-Clad Plate manufacturing process, mechanical tests, cyclic temperature and pressure tests and corrosion tests, all performed using various clad composites. Fabrication techniques for both new and retrofit FGD construction are detailed as well as typical costs using various clad

composites. In addition a detailed list of users and installations will be presented.

8:50 AM

THE APPLICATION OF TITANIUM AERO TECHNOLOGY TO COMPACT HEAT EXCHANGER MANUFACTURE: *Dr. John O. Fowler*[1]; [1]Rolls Royce and Associates Ltd, Derby England

Both superplastic forming (SPF) and diffusion bonding (DB) of alloy titanium have been developed by Rolls Royce plc for application in critical aero engine components, most notably the wide chord hollow fan blade for the new generation of TRENT engines. These technologies have been utilized in the development of a new type of plate/fin heat exchanger, for arduous offshore duty, which offers a compact, lightweight, low media inventory solution to a wide range of heat management problems. This paper describes the advantages of the new product, together with the design and manufacturing concepts developed as part of the technology transfer process.

9:10 AM

TITANIUM IN THE DESALINATION AND POWER INDUSTRIES: *Mr. Don M. McCue*[1]; [1]TIMET, Old Lyme, CT 06371

Titanium tubes missed the big surge in desalination plants and first generation nuclear power plants, in the early 1960's. The primary reasons were availability and cost since only seamless tube was being manufactured. However, by the early 1970's welded tube in several grades was available in relatively large quantities and production capacity was easily increased as the demand grew in second generation nuclear plants and for retubing older fossil and nuclear power plants. The 1970's also saw the beginning of the huge desalination plant program in Saudi Arabia where titanium tubes were specified for both the desalination units and the supporting power plants. Titanium tubes were also specified in the ill-fated Ocean Thermal Energy Concept (OTEC) which was to generate electric power using the thermal difference between surface ocean water and the temperature 300 feet below. The motive fluid was to be ammonia. The paper will deal with the reasons why titanium was the material chosen for each of these three applications.

9:30 AM

RESISTA-CLAD TITANIUM IN THE CHEMICAL PROCESS INDUSTRIES: *Mr. Kenneth W. Bird*[1]; [1]SPF Corporation of America, Louisville, CO 80027

The use of titanium in the Chemical Process Industries is increasing because engineers are becoming more knowledgeable and sensitive to the ability of the material to withstand the corrosive attack of aggressive organic and inorganic media. Because of the initial cost of titanium and other reactive metals like zirconium, niobium and tantalum, a process was developed to apply these materials in thickness' from 0.5mm to 2.0mm to a structural base metal like carbon steel. The alternative is to utilize solid materials from 6.0mm in thickness and greater depending upon mechanical considerations, or explosion clad product using a minimum thickness of 3.0mm applied to a structural base material. Applications in the chemical, pulp and paper, fine chemical, food, an d pharmaceutical industries will be addressed. History, examples and engineering information will be provided as well.

9:50 AM

TITANIUM/STEEL EXPLOSION BONDED CLAD FOR HYDROMETALLURGY AUTOCLAVES: *Mr. John G. Banker*[1]; [1]Clad Metal Products, Inc, Boulder, CO 80301

Titanium is the material of choice for many highly corrosive reactor and autoclave applications. Titanium provides superior corrosion protection in autoclaves for pressure acid leaching and pressure oxidation leaching of metal ores. Clad metal construction offers a significant cost reduction for equipment of this type. Titanium alloys can be selectively applied in specific areas of the autoclave to accommodate local environmental conditions. Considerations in alloy selection and clad fabrication are discussed in detail. Recent experience in titanium clad autoclave construction is reviewed.

10:10 AM

THE APPLICATION OF TITANIUM AND IT'S ALLOYS IN THE ANODIZATION OF ALUMINUM: *Mark A. Ormiston*[1]; [1]Anomatic Corporation, Newark, OH 43055

The electrochemical anodization of aluminum has been an important method of improving the performance and finish of many types of aluminum components. The jigs or fixtures used to convey the aluminum parts through the particular chemical baths associated with the process have historically been made of several different metals. The acid based composition of the chemical baths as well as the electrical nature of the process preclude the use of many materials to fixture the aluminum parts. Titanium has been selected by many in the industry due to it's inherent chemical resistance and electrical conductivity. A brief history of the industry will be discussed with some of the background relating to the choice of materials. A case history of a unique application of titanium in the anodizing industry will be presented. This application utilizes a strip of titanium fashioned into a continuous conveyor belt. Interchangeable tooling, also made from titanium, is attached to the conveyor belt to hold the aluminum pieces as the conveyor moves through the various chemical baths. This anodizing system is optimized for the high production of a variety of small aluminum pieces. Chemical as well as physical specifications of the titanium used in the processing machinery along with the operating parameters of the equipment will be discussed.

10:30 AM

INCREASE OF LIFETIME OF THE TITANIUM VALVES FOR AGGRESSIVE ABRASIVE MEDIUMS BASED ON CREATION OF RESIDUAL COMPRESSIVE STRESSES ON ITS STEM.: *Alexey Lozhko*[1]; Igor Mezhebovsky[2]; [1]State Metallurgical Academy of Ukraine, Department of Heat Technology and Environment Engineering, 4 Gagarin Prosp. Dniepropetrovsk UA-320635 UKRAINE; [2]Promarmatura Inc., 6 Dzerzhinsky Str Dniepropetrovsk UA-320635 UKRAINE

Usually titanium products for pipelines have more prime cost than similar steel. That is why increase of its lifetime is very important for the buyers. There are many difficult and expensive technologies for improvement of microstructure. Our approach is based on creation of residual stresses. For development of particular technologies we use the original software which controls the thermal-mechanical-chemical processes during heat treatment. The example shows the distribution of the axial stresses in a valve, the stem of which should be in aggressive abrasive medium. The reason of valve stem fragility in such conditions is a microcrack on its surface. Such microcracks become the centers of destruction. If residual compressive stresses are created on the stem surface, the microcracks do not propagate. The valve stem surface acquires a resistance to chemical and mechanical destruction. Durability of such a valve is therefore considerably higher.

PROCESSING-STRUCTURE-PROPERTY RELATIONSHIPS OF COMPOSITE INTERFACES: SESSION II: INTERFACES IN TITANIUM MATRIX COMPOSITES

Sponsored by: Jt. ASM International: Materials Science Critical Technology Sector/Structural Materials Division, Composite Materials Committee, Materials Design & Manufacturing Division, Powder Materials Committee

Program Organizers: Sunil G. Warrier, UES, Inc., 4401 Dayton-Xenia Rd., Dayton, OH 45432-1894; Mary Lee Gambone, WL/MLLM, Wright Lab Materials Directorate, WPAFB, OH 45433; Ray Y. Lin, University of Cincinnati, Dept. of Materials Sci. & Eng., Cincinnati, OH 45221-0012; Benji Maruyama, WL/MLLM, Wright Lab Materials Directorate, WPAFB, OH 45433

Tuesday AM Room: Centro A
February 17, 1998 Location: Convention Center

Session Chairs: Daniel B. Miracle, Wright Laboratory Materials Directorate, Wright-Patterson AFB, OH 45433; Partha Rangaswamy, LANSCE, Los Alamos National Laboratory, Los Alamos, NM

8:00 AM INVITED
DESIGN OF MONOFILAMENT COATINGS FOR TITANIUN MATRIX COMPOSITES: *R. A. Shatwell*[1]; [1]DRA Sigma, BP Research and Engineering Centre, Sunbury, Middlesex TW 16 7LN England

The design of monofilament coatings to give reliable performance of Ti-MMCs must take several factors into account. For example: Reactivity with the matrix, stresses within the coatings before and after consolidation, transverse and axial mechanical properties, and cost. These are illustrated with reference to the development of coatings for Sigma silicon carbide monofilament.

8:45 AM
PROCESSING-STRUCTURE-PROPERTY RELATIONSHIPS FOR CARBON COATINGS ON SILICON CARBIDE FIBERS IN METAL MATRIX COMPOSITES: *K. L. Kendig*[1]; R. Gibala[2]; D. B. Miracle[1]; B. A. Shatwell£[3]; [1]Materials Directorate, Air Force Research Laboratory, Wright-Patterson AFB, OH 45433 USA; [2]University of Michigan, Dept. of Materials Science and Engineering, Ann Arbor, MI 48109-2136; [3]Defense Evaluation and Research Agency, Sunbury on Thames, Middlesex TW 16 7LN UK

Continuous SiC fibers utilized in Ti-alloy metal matrix composites are often coated with a C-based coating. Results from the literature indicate this coating controls the composite interface failure response in transverse tension. A series of C coatings on SiC fibers were deposited using a systematic variation of a deposition parameter. Transverse mechanical testing of model, single-fiber composites produced with these coated fibers and a Ti-6Al-4V matrix alloy indicates a correlation between coating deposition parameters, coating properties, and composite interface strength. TEM observations were performed to determine the microstructural parameters of the C coatings which are affected by the changes in processing.

9:10 AM
DEVELOPMENT AND CHARACTERIZATION OF INTERFACES FOR OPTIMIZATION OF TMC PROPERTIES: *B. S. Majumdar*[1]; S. G. Warrier[1]; [1]UES, Inc., Dayton, OH 45432

In order to derive optimized longitudinal and transverse properties out of fiber reinforced titanium matrix composites (TMCs), new interface systems are being developed and characterized. One approach being pursued is the concept of a ductile plus barrier metallic layer, such that the needed level of bonding is achieved without any significant degradation of fiber strength. Characterization of the interphase involves both microstructural evaluation, and determination of the transverse normal strength and friction stress under push-out conditions. Also, single-fiber fragmentation tests are conducted to determine the insitu fiber strength, as well as an average shear stress of the interface responsible for load transfer under fragmentation conditions. The performance of the TMC is assessed by fabricating single-ply composites, and testing and modeling the strength and fatigue crack growth behavior under longitudinal loading. The results for the new interfaces will be discussed, along with comparisons of the data with those from single-fiber and single-ply TMCs that have commercial and experimental SiC fibers with carbon coatings. This work was performed at the Materials Directorate, Wright Laboratory, under AF Contract No. F33615-96-C-5258.

9:35 AM Coffee Break in Exhibit Hall

9:50 AM
BEHAVIOR OF SEVERAL INTERFACES DURING FATIGUE CRACK GROWTH IN SiC/TI-6Al-4V COMPOSITES: *S. G. Warrier*[1]; B. Maruyama[2]; B. S. Majumdar[1]; D. B. Miracle[2]; [1]UES, Inc., Dayton, OH 45432; [2]Wright Laboratory, Materials Directorate, Wright-Patterson AFB, OH 45433-7817

Interface optimization is desired to improve the transverse properties without degrading the damage tolerant behavior of continuous fiber reinforced composites. In this study, the effect of the interface on debonding, crack bridging and elastic shielding has been examined for a variety of interfaces with significantly different mechanical characteristics. All composites exhibited crack bridging, the stress range for which was dictated by the type of the interface and the fiber strength. Elastic shielding issues and damage mechanisms during crack growth will be addressed. Results of several newly developed interfaces will also be presented. This research has been performed at the Wright Laboratory Materials Directortate with support from AF Contract F33615-96-C-5258.

10:15 AM
TRANSVERSE TENSILE AND FATIGUE CRACK GROWTH BEHAVIOR OF Ti-MATRIX COMPOSITES WITH SPATIALLY VARIED INTERFACES: *Benji Maruyama*[1]; Sunil Warrier[2]; [1]Wright Laboratory Materials Directorate, Wright-Patterson AFB, OH 45433; [2]UES, Inc., Dayton, OH 45432

Spatially Varied Interfaces is a design concept for composite synthesis whereby the interface mechanical response is tailored to the composite needs by varying the interface properties in patterns of weak and strong areas. In the SiCf/Ti-alloy system, the longitudinal fatigue crack growth and transverse tensile behavior have been modified in a controlled manner using the SVI technique. The results of these experiments have enabled a better understanding of the stress states and interface failure mechanisms. This work was conducted in the Metals & Ceramics Division of the Materials Directorate at Wright Laboratory.

10:40 AM
ROLE OF INTERFACE ON FATIGUE BEHAVIOR OF FIBER-REINFORCED TITANIUM AND TITANIUM ALUMINIDE MATRIX COMPOSITES: *Y. C. Her*[1]; P. C. Wang[1]; J.-M. Yang[1]; [1]University of California, Department of Materials Science and Engineering, Los Angeles, CA 90024-1595 USA

The role of fiber/matrix interface on fatigue behavior of several fiber-reinforced titanium and titanium aluminide matrix composites under low cycle fatigue loading was investigated. The materials systems evaluated in this work include SCS-6Ti-15-3, SCS-6/Ti-6-4, SCS-6/Ti-24-11, Ag/Ta coated SCS-6/Ti-25-10 and SCS-6/Ti-22-23 composites. The effect of fiber surface coating and interfacial reaction layer on fatigue behavior, including fatigue damage evolution, stiffness degradation and crack propagation patterns will be discussed. Analytical models for predicting the effect of interfacial conditions on fatigue behavior of these materials will also be presented.

11:05 AM
EFFECT OF ELEVATED TEMPERATURE EXPOSURE ON THE INTERFACIAL PROPERTIES OF SCS-6/BETA-21S COMPOSITE: *C. R. Ananth*[1]; J. Watts[1]; N. Chandra[1]; [1]Florida State University, Department of Mechanical Engineering, Tallahassee, FL 32310

Fiber-matrix interface plays a critical role in the performance of Titanium Matrix Composites. The size and composition of the reaction zone at the interface affects the mechanical properties of the interface. Post-processing heat treatment is one of the ways to modify the interfacial conditions. In this study, SCS-6/Beta-21s metal matrix composite is exposed to near consolidation as well as other temperatures closer to service conditions, for varying periods of time. The thickness of the reaction zone and reaction products are evaluated using metallurgical techniques. Fiber push-out and fragmentation tests are used to characterize the mechanical properties of the interface. A novel computational method is used to simulate the propagation of interfacial cracks during the tests. The fracture toughness of the interface is evaluated from the experimental data using this model. A relationship between the temperature and the time of exposure to changes in mechanical and fracture properties of the interface is established.

RAPID SOLIDIFICATION: MODELING & EXPERIMENTS: Dendrite Growth Velocity

Sponsored by: Materials Design and Manufacturing Division, Solidification Committee

Program Organizers: W. Hofmeister, Vanderbilt University, P.O. Box 1543 Station B, Nashville, TN 37235; R. Trivedi, Iowa State University, 100 Wilhelm Hall, Ames, IA 50011

Tuesday AM Room: Plaza Room D
February 17, 1998 Location: Convention Center

Session Chair: William Hofmeister, Vanderbilt University, Nashville, TN 37235

8:30 AM INVITED
NUCLEATION AND GROWTH OF METASTABLE PHASES IN UNDERCOOLED MELTS OF METALS AND SEMICONDUCTORS: *Dr. Dieter Matthias Herlach*[1]; [1]German Aerospace Research Organization, Institut fuer Raumsimulation, D-51170 Koeln 51170 Germany

Electromagnetic levitation technique is applied to undercool bulk melts far below their melting temperatures. An undercooled melt corresponds to a non-equilibrium state which gives access to the solidification of a great variety of metastable solids. Nucleation of materials of quasicrystalline and different crystalline structures is studied. Nucleation selects the crystallographic phase stable or metastable. The crystallization process is completed by subsequent growth. Crystal growth in undercooled melts takes place via dendritic growth. Measurements of dendrite growth velocities are presented whose analysis within current theories allows a detailed understanding of non-equilibrium processes during rapid solidification of a deeply undercooled melt. Deviations from the chemical equilibrium at the interface leads to the crystallization of metastable supersaturated phases. An interface undercooling is favorable for the formation of disordered superlattice structure in intermetallic compounds. Transitions in the morphology of semiconductors are observed. The undercooling also controls the transition from coarse grained dendritic to grain refined equiaxed microstructure. Finally, recent experiments are presented giving evidence for magnetic ordering in undercooled melts of CoPd alloys.

9:15 AM INVITED
TESTS OF THEORIES FOR NONPLANAR GROWTH DURING RAPID ALLOY SOLIDIFICATION: *Dr. Michael J. Aziz*[1]; [1]Harvard University, Div. of Engrg. & Appl. Sci., Cambridge, MA 02138 USA

During rapid solidification, kinetically suppressed solute partitioning at the crystal/melt interface, as well as kinetic interfacial undercooling, become important. Both of these effects are expected to have significant stabilizing influences on a planar interface during rapid solidification. We will present experimental tests of models for the transition from planar to cellular growth, and for the velocity-undercooling function of the dendrite tip, in the velocity regime where nonequilibrium interface kinetics are important.

9:55 AM Coffee Break in Exhibit Hall

10:05 AM INVITED
THE MEASUREMENT OF DENDRITE TiP PROPAGATION VELOCITY DURING GROWTH INTO UNDERCOOLED METALLIC MELTS: *Dr. Douglas M. Matson*[1]; [1]Massachusetts Institute of Technology, Materials Science & Engineering, Cambridge, MA 02139 USA

High speed digital imaging is a novel technique which is currently being used to shed new light on understanding the development and evolution of solidification structures during recalescence from undercooled metallic melts. Rejection of the heat of fusion from the dendrite tip into the liquid results in local thermal gradients which have been successfully imaged as growth progresses across the exposed surfaces. By tracking the steady-state propagation of this interface, bulk growth velocities may be evaluated and the morphology of the underlying dendritic array may be predicted. Results of this work support classic growth theory at low undercoolings and highlight the need for developing an improved model to describe global macrostructural solidification behavior and the potential for interaction between individual dendrites within the array - especially at high undercoolings.

10:45 AM INVITED
EXAMINATION OF EXPERIMENTAL SOLIDIFICATION VELOCITY MEASUREMENTS IN RELATION TO DENDRITIC GROWTH THEORY: *Dr. Bryan Timothy Bassler*[1]; Dr. Robert J. Bayuzick[2]; Dr. William H. Hofmeister[2]; [1]Materials Resources International, Research and Development, North Wales, PA 19454 USA; [2]Vanderbilt University, Nashville, TN 37235 USA

Comparison of dendritic growth theories to experimental measurements of the solidification velocity as a function of undercooling indicates both the strengths and weaknesses of the theories and the measurements. Qualitative agreement to experimental results is exhibited for low undercoolings and low solute concentrations. However, the theories do not correctly predict the behavior of these materials at large undercoolings. For higher solute concentration alloys there are no areas of agreement between theory and experimental results. The most significant observation that can made from the comparison of measured solidification velocities to the predictions of dendritic growth theory is the fact that collision limited growth is an incorrect assumption for bulk metallic systems. Additionally, observations based on the comparison can be made about the marginal stability parameter, the kinetic parameter, and solute trapping. These aspects of dendritic theory, along with a brief examination of errors in experimental measurements, will be addressed.

11:25 AM
DETERMINATION OF VELOCITY-UNDERCOOLING RELATIONSHIPS IN Cu AND Cu-O MELTS BY THE MELT ENCASEMENT TECHNIQUE: *Dr. Robert F. Cochrane*[1]; Ms. Sharon E. Battersby[1]; Dr. Andrew M. Mullis[1]; [1]University of Leeds, Department of Materials, Leeds LS2 9JT U.K.

A melt encasement (fluxing) technique has been used to systematically study the velocity-undercooling relationships in samples of Cu and Cu-O at undercoolings of up to 250 K. The apparatus was designed such that it was possible to view the sample throughout the experiment, allowing solidification velocity measurements to be made. These velocity measurements were subsequently correlated with the as-solidified microstructures. In pure Cu, the solidification velocity increased

smoothly with undercooling up to a maximum of 85 m/s at 250 K. No evidence of grain refinement was found in any of the as-solidified samples. However, in Cu doped with 200 ppm of oxygen, we found that samples undercooled by more than 190 K had a grain refined microstructure and that this corresponded with a clear discontinuity in the velocity-undercooling curve. Grain refinement was also observed at undercoolings below 100 K, but in this case there was no obvious signature in the velocity-undercooling relationship.

REACTIVE METALS—GENERAL SESSIONS: Reactive Metals — General Session I

Sponsored by: Light Metals Division, Reactive Metals Committee
Program Organizer: John N. Hryn, Argonne National Laboratory, 9700 S. Cass Ave. Bldg. 32, Argonne, IL 60439

Tuesday AM Room: 209
February 17, 1998 Location: Convention Center

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

8:30 AM
THERMODYNAMICS MODELING OF REACTIVE METAL SYSTEMS: *R. S. Chiou*[1]; P. T. Velu[2]; R. G. Reddy[2]; [1]The University of Alabama, Department of Chemical Engineering, Tuscaloosa, AL 35487;2 The University of Alabama, Department of Metallurgical & Materials Engineering, Tuscaloosa, AL 35487-0202

Production of neodymium metal by the reduction of neodymium salts with calcium and sodium as reductants in the presence of fluxing agents consisting of salts like $CaCl_2$ and NaCl was studied. Thermodynamic calculations using a Gibbs energy minimization method was carried out to characterize the process. The effect of various parameters, such as temperature, pressure, and salt composition, on the yield and impurities content of the product have been analyzed. The yield of Nd increased with increases in temperature and fluxing agents and so did the impurity content of the alloy. The calculated data show an excellent agreement with large scale experimental data.

9:00 AM
KINETICS OF CHLORINATION OF CHROMITE: N. Kanari[1]; *I. Gaballah*[1]; [1]Mineral Processing and Environmental Engineering, ENSG-LEM, 54501 Vandoeuvre Cedex France

Chlorination can be an efficient alternative for the physical beneficiation of refractory metals' bearing materials. The chlorination of a chromite mineral was studied up to 1000°C using thermogravimetric analysis. The effects of the gas flow rate, temperature and partial pressure of the reactive gases on the reaction rate were studied in isothermal conditions. Only $FeCr_2O_4$ could be chlorinated up to 1000°C by Cl_2+O_2 and Cl_2+N_2 gas mixtures generating chromium oxychloride (CrO_2Cl_2) that can be recovered by cooling the gas phase. The oxychlorination can ameliorate the characteristics of chromite bearing materials and/or the recovery of the chromium compounds from its wastes.

9:30 AM
CHARACTERIZATION AND PURIFICATION OF A PHOSPHOROUS CONTAINING SCHEELITE ORE CONCENTRATE: *Raj P. Singh*[1]; Michael J. Miller[1]; [1]ORSAM SYLVANIA Products Inc., Research and Development Division, Chemical Development Department, Towanda, PA 14848 USA

Mineralogical characterization and purification of a scheelite ore concentrate containing about 50% $CaWO_4$, 35% $CaCO_3$, 12% $Ca_{10}(PO_4)_6(OH)_2$ and 3% SiO_2 will be reported in this paper. In addition to these major phases, the ore concentrate also contained trace amounts of toxic elements such as arsenic, lead, and uranium, which were associated with the apatitic part of the ore. During the removal of phosphorous in HCl (required before the processing of such ores for tungsten) these elements reported to the solution. In acidic solution, P and As may be present as heteropoly anions of W, such as $PW_{12}O_{40}^{3-}$ and $AsW_{12}O_{40}^{3-}$, formation of which would provide some driving force for unwanted dissolution of $CaWO_4$ in HCl. The loss of W and expensive disposal of toxic (and radioactive) solutions will add extra cost in the processing of such ores. A "Design Of Experiment" (DOE) approach was used to study the purification of ore concentrate in HCl. These results and mineralogical characterization of the ore concentrate will be discussed.

10:00 AM Coffee Break in Exhibit Hall

10:30 AM
CORROSION OF NON-FERROUS MATERIALS IN LIQUID LITHIUM AND LITHIUM CHLORIDE: *D. L. Olson*[1]; B. Mishra[1]; C. S. Eberle[2]; [1]Colorado School of Mines, Department of Metallurgical & Materials Engineering, Golden, Colorado 80401-1887 USA; [2]Argonne National Laboratory-West, Idaho Falls, ID 83403-2528 USA

Several non-ferrous materials have been considered over the years as containment material for lithium and lithium halides. Surface modified refractory metals are being extensively investigated. An overview of experimental observations and results of liquid lithium corrosion of selected engineering non-ferrous materials will be presented. The nature of the degradation and its mechanism will be explained. The influence of temperature, microstructure, stress, impurities and service time on the corrosion behavior for various engineering alloys will be discussed. The state of the mechanistic understanding of the corrosion process will be given. Selection rules for materials of containment for liquid lithium and lithium compounds shall be suggested.

11:00 AM
NEW ENVIRONMENTALLY FRIENDLY PROCESSES FOR THE PRODUCTION OF REFRACTORY METALS BY METALLOTHERMIC REDUCTION: Toru H. Okabe[1]; *Donald R. Sadoway*[1]; [1]Massachusetts Institute of Technology, Department of Materials Science and Engineering, Cambridge, MA 02139-4307 USA

Metallothermic reduction is used in the primary extraction of many metals, including titanium, zirconium, beryllium, neodymium, and tantalum. The commonly held view is that metallothermic reduction is strictly a chemical reaction and that the process is rate limited by mass transfer. In a study of the production of tantalum powder by the reaction of K_2TaF_7 with sodium, we have shown that there are two dominant kinetic pathways - both involving electron transfer. Thus, metallothermic reduction is an "electronically mediated reaction" and not a simple chemical reaction. The results can be generalized to design environmentally friendly processes using cheap reductants previously avoided for fear of contamination of the metal product, e.g., scrap aluminum for the production of titanium.

11:30 AM
SYNTHESIS AND CHLORINATION OF MANGANO-COLUMBITE BY MEANS OF A SOLID-FLUID REACTION: J. Gonzalez[1]; J. Rivarola[1], *M. del C. Ruiz*[1]; [1]Instituto de Investigaciones en Tecnologia Quimica (UNSL-CONICET) C.C. 290, 5700 San Luis, Argentina
Abstract Not Available

STRENGTHENING IN HIGH TEMPERATURE INTERMETALLICS: STRENGTHENING IN HIGH TEMPERATURE INTERMETALLICS III: Nickel Aluminides

Sponsored by: Structural Materials Division, Mechanical Metallurgy Committee

Program Organizers: Young-Won Kim, UES, Inc., Materials & Proc. Division, Dayton, OH 45432-1805; Michael J. Kaufman, University of Florida, Dept. of Materials Sci & Eng., Gainesville, FL 32611-2066; Chain T. Liu, Oak Ridge National Lab, PO Box 2008 Bldg 4500S, Oak Ridge, TN 37831-6115

Tuesday AM Room: 107
February 17, 1998 Location: Convention Center

Session Chairs: Michael J. Kaufman, University of Florida, Dept of Matls Sci & Engrg, Gainesville, FL 3261; Sung H. Whang, Polytechnic University, Department of Chemical Engineering, Brooklyn, NY 11201

8:30 AM

ELECTRON MICROSCOPY STUDIES OF STRAIN AGING BEHAVIOR IN SINGLE CRYSTAL NiAl: *Prof. Martin A. Crimp*[1]; B-C. Ng[1]; B. Ghosh[1]; [1]Michigan State University, Dept. of Materials Science and Mechanics, East Lansing, MI 48824 USA

In an effort to understand the details of the well known strain aging phenomenon in NiAl, dislocation generation and motion have been studied in both commercially pure and high purity stoichiometric single crystals using a number of complimentary electron microscopy techniques. In-situ tensile straining has been performed using transmission electron microscopy (TEM) in order to evaluate the mobility of dislocations as a function of alloy purity and thermal history. The mobile dislocations have consequently been evaluated for active slip planes and Burgers vectors. Direct imaging of dislocations in bulk specimens has been performed using electron channeling contrast imaging (ECCI) in scanning electron microscopy. These experiments have examined the dislo cation distributions at crack tips and along crack edges in in-situ deformed 4-point bend specimens. This has revealed significant differences in the toughening characteristics of commercial and high purity NiAl. This research has been supported by the Office of Naval Research (Grant No. N00014-94-1-0204).

9:00 AM

CREEP STRENGTHENING IN NiAl-Cr DIRECTIONALLY SOLIDIFIED EUTECTICS: *Prof. Tresa M. Pollock*[1]; Dr. Dakshinamurthy V. Kolluru[1]; [1]Carnegie Mellon University, MSE Department, Pittsburgh, PA 15213 USA

Creep experiments, electron microscopy and numerical modeling have been utilized to identify creep strengthening mechanisms active in directionally solidified (DS) eutectics. The creep deformation characteristics of DS NiAl-Cr eutectics containing 30 vol% Cr fibers has been studied for longitudinal and transverse loading conditions at 1000ºC. Over a wide range of applied stresses and creep strains, the Cr fibers remain dislocation-free, providing composite strengthening similar to that observed in synthetic composites. However, in the later stages of longitudinal deformation, as stresses in the fiber rise to high levels due to load transfer, interfacial dislocation networks provide sources of dislocations for fiber deformation. To assess the contribution of matrix creep to the two phase deformation problem, single phase single crystals of NiAl and NiAl containing 2% Cr in solution have also been subjected to creep deformation. Solid solution strengthening of the matrix provides a large contribution to the overall creep resistance of the composite. Finite element models which have taken the above mechanisms into account, explain the experimentally observed creep behavior satisfactorily.

9:30 AM

SOLID SOLUTION STENGTHENING IN SINGLE CRYSTAL $NiAl_{45}BE_5$: *Dr. Robert J Hanrahan, Jr.*[1]; R. D. Field[1]; F. Chu[1]; L. A. Jacobson[1]; D. J. Thoma[1]; M. J. Kaufman[2]; J. D. Whittenberger[3]; R. D. Noebe[3]; [1]Los Alamos National Laboratory, Materials Science and Technology, Los Alamos, NM 87545 USA; [2]University of Florida, Dept. of Materials Science and Engineering, Gainesville, FL 32611 USA; [3]NASA Lewis Research Center, Cleveland, OH 44135 USA

In NiAl, beryllium substitution for aluminum can be achieved at alloying levels up to at least 7 a/o. In this study a single crystal of nominal composition 50% Ni, 45% Al, 5% Be was grown via the Bridgman technique. A variety of properties have been measured, including thermal expansion with dilatometry, elastic properties with resonant ultrasound spectroscopy, and hardness with microindentation. The latter results indicated significant solid solution strengthening due to the Be addition compared to binary NiAl. Consequently, oriented single crystal samples were tested in tension at 573-1173 K. In addition, constant rate compression tests were conducted on [001]-oriented compression samples at 1200-1400K and strain rates of $1x10^{-4}$ to $2x10^{-7}$. Compared to high purity single crystal NiAl, the Ni(Al,Be) solid solution single-crystal alloy exhibited significant improvements in strength over the entire temperature range tested. For example, in tensile tests at 1273 K, the samples had a yield strength of 375 MPa (as compared to 30 MPa for NiAl) with 75 % elongation to failure. Moreover, the compression creep data show that Be alloying decreases the strain rate by three orders of magnitude at a stress level of 50 MPa in crystals oriented in the [001] direction.

9:50 AM

THE EFFECT OF STRESS ON THE MICROSTRUCTURAL STABILITY OF NiAl-Mo EUTECTICS DURING THERMAL FATIGUE: *Matthew Thomas Kush*[1]; Dr. Ronald Gibala[1]; Dr. John W Holmes[1]; [1]University of Michigan, Materials Science, Ann Arbor, MI 48109-2136 USA

The microstructural stability of the directionally solidified eutectic NiAl-9 at% Mo was investigated by subjecting disk-shaped specimens to thermal fatigue conditions. Two different microstructures, cellular and non-cellular, produced by different processing conditions, were evaluated for stability and strength. Thermal fatigue tests were at elevated temperatures by induction heating disk-shaped specimens in an argon gas atmosphere using time-temperature heating and cooling profiles to approximate potential engine applications. These results were compared to ones obtained from constant-stress creep tests. To quantify microstructural changes, the fiber size, fiber size distribution and fiber density were measured as a function of time at temperature for each of the processing conditions. The overall results demonstrate that the cellular microstructures are more stable under thermal cycling or creep conditions than the non-cellular microstructures.

10:10 AM

STRUCTURE/PROPERTY RELATIONSHIPS IN NiAl ALLOYS CONTAINING Zr AND Si: *Mr. Manas Lakshmipathy*[1]; Mr. Yongjin Lim[1]; Dr. Padmavardhani Durbha[1]; Dr. Michael J. Kaufman[1]; [1]University of Florida, Dept. of Materials Science and Engineering, Gainesville, FL 32611 USA

The effects of Zr and Si on the microstructure and mechanical properties of near β-NiAl alloys has been investigated. While it is known that the G ($Ni_{16}Zr_6Si_7$) phase tends to be a more potent strengthener than either the Heusler (Ni_2AlZr) or Laves (NiZrSi) phases in this system, the relative stabilities as a function of composition remain uncertain. In this study, the stability, morphology and distribution of G phase has been examined by varying both the composition and the thermal history of the alloys. It is shown that increasing the Ni, Zr, and Si contents appears to lead to both a relatively high volume fraction of the G phase and to increase its thermal stability with respect to transforming into t he other phases. Compression tests at 1300K and strain rates in the range of 10^{-3} - 10^{-5} s^{-1} were performed in order to determine the effects of G phase on the high temperature strength of NiAl. The various results will be discussed with respect to the potential

for strengthening intermetallics in general and NiAl in particular. (The authors acknowledge the support of the Air Force Office of Scientific Research (URI Grant F49620-93-0309) under the direction of Dr. Charles H. Ward.)

10:30 AM

STRENGTHENING IN A DS CAST Ni_3AlBASER ALLOY IC6 FOR AERO-ENGINE TURBINE VANES: *Prof. Yafang Han*[1]; Zhanping Xing[1]; Chengbo Xiao[1]; [1]Inst. of Aeronautical Materials, Beijing 100095 China

A directionally solidified casting Ni3Al base alloy, named Alloy IC6, has been recently developed at Beijing Institute of Aeronautical Materials. The alloy not only has high strength and ductility from room temperature to 1200°C, excellent creep resistance over a wide temperature range of 700°C to 1100°C, but also shows very good thermal cycle fatigue resistance and high incipient melting point (Tm=1310-1320°C), which are very important for aero-engine turbine vanes. The microstructural observations and analysis indicate that the superior mechanical properties of this alloy may be attributed to solid solution hardening by large molybdenum addition, second-phase strengthening by γ phase and other minor phases that precipitate in various temperature ranges, the formation of a γ raft structure during creep, and to the existence of high-density misfit dislocation networks at γ'/γ interface areas due to a high value of γ'/γ misfit. Alloy IC6 has been successfully applied for turbine vanes of an advanced aero-engine and passed 250h engine tests as well as 30 taking off/landing cycles and 15 flight hours.

11:00 AM

STRENGTHENING AND TOUGHENING OF $L1_2$-ORDERED γ ′-PHASE BY PRECIPITATES OF THE DISORDERED FCC γ-PHASE: *Dr. Wei Liu*[1]; Mr. Thorsten Krol[1]; Prof. Dr. Eckhard Nembach[1]; [1]Universität Münster, Institut für Metallforschung, D-48149 Münster Germany

Homogeneously distributed precipitates of the disordered fcc γ-phase can be obtained in a series of $L1_2$-ordered γ ′-intermetallics in the $(Ni,Co)_3(Al,Ti)$, $(Ni,Co)_3(Si,Ti)$ and $Ni_3(Si,Al,Ti)$ alloy systems. Because of the attractive interactions between the superdislocations of the γ ′-matrix and the disordered γ-precipitates, the γ ′-intermetallics are significantly strengthened as compared to monolithic γ ′-intermetallics such as Ni_3Al and Ni_3Si. On the other hand, the toughness of the studied γ ′-intermetallics is also improved due to the presence of a ductile γ-phase (reduction of the crack propagation velocity) as well as due to the Ni- or Co-rich deviation of the γ ′-matrix from the stoichiometry (modification of grain boundaries). The present work is designed to investigate the strengthening and toughening of the γ-precipitate-containing γ ′-intermetallics by hardness measurements, by compression and tensile testing as well as by TEM and SEM examinations. Mechanical properties such as the flow stress, the ultimate strength and the plastic elongation of the γ′-intermetallics were measured and related to the γ-precipitates size, volume fraction, shape and distribution in the γ ′-matrix. The fracture modes were analyzed and discussed in terms of alloy composition, microstructure and testing conditions.

11:20 AM

DUCTILITY OF Ni_3Al SINGLE CRYSTAL AT ELEVATED-TEMPERATURE EFFECT OF PREOXIDATION: *Dr. Zhigang Xiao*[1]; R. H. Zee[1]; [1]Auburn University, Materials Research and Engineering Center, Auburn, AL 36849 USA

Ni3Al alloys are generally resistant to air oxidation as a result of their ability to form adherent oxide surface scales that protect the base materials from further attack. However, environmental embrittlement in single crystal Ni3Al alloys at elevated temperatures in oxidizing environments is not fully understood. In order to elucidate this aspect, a tensile testing was conducted on preoxidized binary Ni3Al (23.5at.%Al) single crystals which were preoxidized in a tube furnace at elevated temperatures in air for 20 h before tested at the same temperatures as that used for preoxidation in each case. The tensile specimens gage dimension is 8 x 3 x 1 mm3. The strain rate was 0.5 x 10-3 s-1. The orientations of the specimens are in <210> according to X-ray diffraction analysis. The oxide surface scales thickness is about 5~7 μm. The results indicate that the oxide scales does not affect the strength and ductility of Ni3Al single crystals at elevated temperatures. And, the crystals still maintained anomalous behavior with the maximum yield strength occurring at abo ut 700°C. The mechanisms and kinetics involved in these results will be discussed comprehensively.

11:40 AM

AN INVESTIGATION OF THE EFFECTS OF LAYER THICKNESS ON THE DUCTILE PHASE TOUGHENING OF NICKEL ALUMINIDE COMPOSITES: M. Le[1]; F. Ye[1]; *W. O. Soboyejo*[1]; [1]Ohio State University, Department of Materials Science and Engineering, Columbus, OH 43210

This paper examines the effects of layer thickness on the ductile phase toughening of NiAl composites. Layered NiAl composites with fracture toughness levels between 25 and 35 MPa Vm are engineered by ductile phase reinforcement with V, Mo and Nb-15Al40Ti layers. Resistance curve behavior at room-temperature is shown to occur primarily as a result of crack-tip shielding due to crack bridging and crack-tip blunting mechanisms. However, the bridging zones are degraded under cyclic loading conditions. The microstructural requirements for toughening are also elucidated for crack growth under monotonic and cyclic loading conditions.

SUPERPLASTICITY AND SUPERPLASTIC FORMING: Session III - Superplastic Behavior in Light Alloys

Sponsored by: Materials Design and Manufacturing Division, Shaping and Forming Committee

Program Organizers: Amit K. Ghosh, Univ of Michigan, Dept. of Matls Sci & Eng., Ann Arbor, MI 48109-2136; Thomas R. Bieler, Univ of Michigan, Dept of Matls Sci & Mechanics, Lansing, MI 48824-1226

Tuesday AM Room: 106
February 17, 1998 Location: Convention Center

Session Chair: Wilbur Simmons, Army Research Office, Research Triangle, Durham, NC

8:30 AM INVITED

SUPERPLASTICITY IN CONVENTIONAL COARSE-GRAINED 6061 AL AND THE LIQUID PHASE EFFECT: *T. G. Nieh*[1]; D. R. Lesuer[1]; R. Kabyshev[2]; [1]Lawrence Livermore National Laboratory, Livermore, CA; [2]IMSP, Ufa Russia

Over the last decade, superplasticity at high strain rates (> 10-1s-1) has been reported in many fine grain structural materials, including Al-base and Mg-base composites, mechanically-alloyed materials, and modified conventional alloys. Many recent experimental evidence suggests that the presence of a small amount of liquid phase at interfaces or grain boundaries not only enhances the strain rate for superplasticity but also has a strong influence on the deformation mechanisms. In the present paper, high temperature properties of conventional 6061 Al (grain size ~ 200 μm) are examined. Experimental results indicate that the ductility of the alloy depends upon both strain rate and temperature. The optimal tensile elongation (350%) was, in fact, obtained at 10-4s-1 and 600°C, slightly above the solidus temperature of the alloy. Microstructure-superplastic property relations for the alloy are characterized and discussed. The role of liquid phase on ductility is particularly emphasized.

8:55 AM

A COMPARISON OF SUPERPLASTIC DEFORMATION IN SEVERAL ALUMINUM ALLOYS: *D. R. Lesuer*[1]; R. Vandervoort[1]; C. Syn[1]; T. G. Nieh[1]; K. R. Brown[2]; H. Yang[2]; R. Kaibyshev[3]; [1]Lawrence Livermore National Laboratory, Livermore, CA; [2]Kaiser Aluminum -

Center for Technology, Pleasanton, CA; [3]Institute for Metals Superplasticity Problems, Ufa Russia

Superplasticity has been observed in a number of 2xxx, 5xxx and 7xxx series aluminum alloys. However, the deformation behavior and cavitation characteristics of these various alloys can vary dramatically. In this presentation we report on a study of the microstructures as well as the deformation and cavitation response of the following commercial or near-commercial sheet aluminum alloys - 5083, 7475, 2124, 2424 and 2219. The deformation response under uniaxial tension and biaxial tension will be compared . At comparable microstructures and temperatures, the superplastic deformation behavior can be divided into two classes - those alloys exhibiting high strain rate sensitivity (e.g., 5083) and those alloys exhibiting a higher strain rate sensitivity (e.g., 7475). In addition, the strain distributions and forming limits during gas pressure forming for the various alloys with different strain rate sensitivities will be compared. Results illustrate the dominant influence of both strain rate sensitivity and cavitation behavior on successful forming.

9:15 AM

THE EFFECT OF GRAIN SIZE ON SUPERPLASTIC BEHAVIOR OF 5083 Al: *D-H Bae*[1]; A. K. Ghosh[1]; [1]University of Michigan, Department of Materials Science and Engineering, Ann Arbor, MI 48109-2136

To understand the effect of grain size on superplastic deformation behavior, stress-strain rate relationship of an Al-Mg alloy has been characterized by conducting an improved multi-step strain rate change test method to preserve near isostructural conditions during the test over the temperature range of 450-550°C. The grain size of the alloy was varied in the range of 8-30 μm by varying thermomechanical processing conditions. A sigmoidal relationship between stress and strain rate is observed unequivocally in each case, which is therefore not a result of concurrent grain growth. Grain size exponent (p) is found as 0.37 in high strain rate region based on a semi-empirical creep equation. This small grain size dependence has not been clearly identified in the literature. In low and intermediate strain rate region, using an effective stress versus strain rate relationship, p is found as 2.07. This result is found to provide good agreement with the model of grain boundary sliding accommodated by the climb of dislocations.

9:35 AM INVITED

SUPERPLASTIC 7050 AND Al-Mg ALLOYS: *D. J. Chakrabarti*[1]; [1]Alcoa Technical Center, Alcoa Center, PA 15069

The development of two proprietary SPF alloys with diverse microstructure, property and industrial applicability are discussed in this paper. The first one relates to the alloy 7050 with an elongation of 600-1100% at 890°F at a strain rate of 0.002-0.01/s, providing one of the best SPF property combinations in metallic alloys produced via ingot route for mass production. 7050 is a stronger alloy and is also less quench sensitive making it a more attractive candidate for aerospace application than the current 7475. The second discussion relates to the development of superplasticity in the low cost Al-Mg alloys at a Mg level lower than the current favorite 4.5 wt% Mg composition (5083 type) for its potential attractiveness in automotive application because of superior corrosion resistance. The SPF properties obtained were quite comparable with those reported for the Al-4.5 Mg alloys. The 7050 and the new Al-Mg alloys displayed widely contrasting microstructure, the implications of which on the evolution and development of superplastic properties in these respective class of alloys will be discussed.

10:00 AM Coffee Break in Exhibit Hall

10:15 AM

SUPERPLASTIC BEHAVIOR OF SUBMICRON GRAIN Al-5083: *J. W. Sinclair*[1]; K. T. Hartwig[1]; R. E. Goforth[1]; D. A. Hardwick[1]; [1]Texas A&M University, Mechanical Engineering Department, College Station, Texas 77843-3123

Commercial Al-5083 (Al-4.7Mg-0.7Mn-0.08Cr) plate was processed to submicron grain (SMG) size using Equal Channel Angular Extrusion (ECAE). Variations in ECAE processing were applied to influence second-phase particle size and distribution and the superplastic response evaluated. Low temperature mechanical data shows ECAE processing which includes intermediate solution heat treatment followed by aging yields higher flow stress and enhanced ductility. Static annealing experiments reveal the SMG microstructure experiences grain growth above 180°C. At elevated temperatures the SMG microstructure becomes highly unstable against grain growth but permits an early window of opportunity for superplasticity.

10:35 AM INVITED

SUPERPLASTIC CHARACTERIZATION OF 2095 Al-Cu-Li-Mg-Ag-Zr ALLOY PROCESSED BY EQUAL CHANNEL ANGULAR EXTRUSION: H. Salem[1]; *R. E. Goforth*[1]; [1]Texas A&M University, Mechanical Engineering Department, College Station, Texas 77843-3123

Several models have been proposed to describe the stress-strain rate behavior of the conventionally processed superplastic pseudo single phase ingot metallurgy (IM) alloys with (2-14 μm) grain size. The most important are the Ashby-Verrall, Ball and Hutchinson and Mukherjee models. A model proposed by O.D. Sherby describes the stress-strain rate behavior for powder metallurgy (PM) materials with (1-10 μm) grain size and mechanically alloyed (MA) materials with (0.3-0.5 μm) submicron grain (SMG) size. The purpose of the research reported in this paper is to develop an understanding of the stress-strain rate behavior of 2095 Al-Cu-Li-Mg-Ag-Zr alloy processed via equal channel angular extrusion (ECAE). A series of thermomechanical processes were employed in order to optimize the processing conditions utilizing ECAE as the primary deformation process for grain refinement. The effect of warm rolling (WR) as a secondary deformation process to ECAE was also investigated. Experimental results for 2095 Al-Cu-Li-Mg-Ag-Zr alloy processed via ECAE and ECAE + WR were compared to the superplastic models proposed by Ashby-Verrall, Ball and Hutchinson, Mukherjee, and Sherby.

11:00 AM

LOW TEMPERATURE SUPERPLASTIC-LIKE BEHAVIOR OF ZK60 MAGNESIUM ALLOY: *H. Watanabe*[1]; T. Mukai[1]; K. Higashi[2]; [1]Osaka Municipal Technical Research Institute, Osaka 536 Japan; [2]Osaka Prefecture University, College of Engineering, Department of Metallurgy and Materials Science, Osaka, 593 Japan

Superplasticity is generally observed at relatively low strain rates (< 10-3s-1) and at temperatures of ~0.7Tm, where Tm is the melting point of the material. Recent advances in material processing for grain refinement have enabled the achieving of superplasticity at high strain rates (= 0.1s-1) or low temperatures. Low temperature superplasticity (LTS) has many advantages over superplasticity at high temperatures. The lower forming temperatures enable reductions in energy costs, tool wear to be made and the oxidation of products. Recently, a fine-grained (3.4 μm) magnesium alloy ZK60 processed by extrusion with high reduction ratio was shown to exhibit high-strain-rate superplasticity at ~0.7Tm. The tensile tests at ~0.5Tm revealed that high ductility was obtained at strain rates between 1 10-5 and 10-3s-1 and the strain rate sensitivity of the flow stress was 0.3. Especially, the maximum elongation of 350% was obtained at a low strain rate of 1 10-5 s-1 and at a temperature of 423K, which is much lower than the majority of superplastic materials reported formerly. The deformation characteristics at ~0.5Tm of ZK60 are discussed by comparing with that at ~0.7Tm.

11:20 AM

LOW TEMPERATURE SUPERPLASTICITY IN A MAGNESIUM ALLOY: *A. Galiyev*[1]; R. Kaibyshev[1]; [1]Institute for Metals Superplasticity Problems RAS, Ufa 450001 Russia

The superplastic behavior of Mg-5.8%Zn-0.65%Zr alloy was considered. In this work, two types of the alloy, with initial grain size 2.5 μm and 1 μm, were examined. Both types exhibit superplasticity in the range of low temperatures t = 125-300°C. The alloy with grain size 2.5 μm shows a maximum superplastic elongation δ= 680% at a strain rate ε= 1.110-4s-1 and t = 250°C. The maximum value of coefficient of strain rate at initial stage of plastic flow was 0.54. Strain increase leads to gradual decrease of "m" value. The surface observations have shown that grain boundary sliding is the dominant deformation mechanism and gives the main contribution to total elongation. The stability of fine grain structure is provided by precipitations of β-phase. Tempera-

ture increase leads to dissolution of this phase. As a result, the superplastic properties drop at t = 300°C. The superplastic behavior at low temperatures of the magnesium alloy is compared with one at higher temperatures. The reasons for low temperature superplasticity are discussed.

ZINC-BASED STEEL COATING SYSTEMS: PRODUCTION & PERFORMANCE: Session III - Performance of Zn-Based Coatings

Sponsored by: Structural Materials Division, Ferrous Metallurgy Committee

Program Organizers: Frank E. Goodwin, Int'l Lead Zinc Research Org., PO Box 12036, Research Triangle Park, NC 27709-2036; Michelle DuBois, Cockerill Sambre, Quai Du Halage 10, Flemalle B-4400 Belgium; Jong-Sang Kim, Pohang Iron & Steel Co. Inc., Kwangyang Research Labs, Chonnam 544 090 Korea; Josef Federl, Voest Alpine Stahl Linz, Turmstrasse 45, PO Box 3, A-4031Linz, Austria; Eduardo A. Silva, USS Technical Center C-20, Monroeville, PA 15146

Tuesday AM Room: Centro Room B
February 17, 1998 Location: Convention Center

Session Chair: Jong-Sang Kim, Pohang Iron & Steel Co. Inc., Kwangyang Research Labs, Chonnam 544 090 Korea

8:30 AM - ORAL ONLY

STONE CHIPPING RESISTANCE AND COATING ROUGHNESS OF GALVANNEALED IF STEELS: *J. Hamers*[1]; A. van der Heiden[2]; W. van Koesveld[2]; J. P. Schoen[2]; [1]Hoogovens Steel Strip Mill Products, Quality Department, CA IJmuiden The Netherlands; [2]Hoogovens Research and Development, CA IJmuiden The Netherlands

Because of its superior anti-corrosion, welding and stamping properties, galvannealed steel sheet (GA) has become an important substrate for automotive inner and outer parts. In order to fully exploit the use of GA Ti+Nb IF steels, an extensive research program has been carried out to achieve a high level of resistance for stone chipping, flaking and powdering, by studying the effect of steel composition and hot-dip galvanizing line process parameters, respectively. Additionally, image clarity demands a control of the coating roughness at longer wavelengths. A sufficient level of interfacial roughness, which can be safeguarded by a high enough strip dip temperature of zinc bath aluminium level, is an effective measure to enhance coating adhesion. Local iron consumption during the formation of Fe, Zn-intermetallics, is the underlying mechanism to create a rougher steel-coating interface. Micro-alloying IF steel with Si, is another way to increase the interfacial strength and thereby the resistance for stone chipping and flaking. In case of high strength steel, P even has a stronger effect. Supported by SEM images, showing similar fracture surfaces, a relation has been established between the lap shear test and the stone chipping test for measuring coating adhesion. A low galvannealing temperature, which is facilitated by a long soaking selection, is beneficial for both powdering and stone chipping resistance. Skin passing decreases the amplitude of the longer wavelengths in the coating surface roughness, while leaving the short wavelengths unaffected. The longer wavelengths are dictated by the roughness profile of the incoming substrate material, whereas craters in the galvanneal coating, caused by outbursts, contribute to the short wavelengths. By removing the coating, it could be shown that the fraction of longer wavelengths in the roughness profile at interface and surface are identical as to position and intensity, both before and after skin passing. Due to the relative hardness of the galvanneal coating, there is a direct transfer of deformation during skin passing to the steel substrate. Crater formation/microroughness is diminished by Si and P in steel substrate, or, if necessary, by lowering the zinc bath aluminium content.

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CORRELATION BETWEEN ADHESION PROPERTIES AND THE INTERFACIAL BONDING STRENGTH OF COMMERCIAL GALVANNEAL COATINGS: *W. Zhong*[1]; H. F. Ng[1]; J. M. James[1]; [1]Dofasco Inc., Research and Development Department, Hamilton, On L8N 3J5 Canada

The adhesion properties of commercial galvanneal coatings on various steel substrates were investigated. The adhesion properties were evaluated by four test methods, including a lap shear test for the interfacial bonding strength, an in-house U-Channel test to simulate the deformation of the coatings during stamping, and the commonly used Double Olsen Cup test and 60° V-bend test. The correlation between the results of these tests was established. The U-channel performance is affected by both the coating ductility and the interfacial bonding strength of the coating. Low bonding strength (i.e.<19 MPa) leads to poor U-Channel performance regardless the ductility of the coating. With high bonding strength, U-channel performance is dominated by the coating ductility. The Double Olsen performance and the 60° V-bend performance are mainly affected by the coating ductility. It was found that low coating Fe content (< 10wt%) and high P content (>0.0.3 wt%) of the substrate result in relatively high bonding strength. The presence of excess Ti in the substrate reduces the bonding strength.

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INFLUENCE OF SURFACE CONDITIONING ON THE FRICTIONAL BEHAVIOR OF HOT DIP GALVANIZED SHEET STEEL: *A. W. Silimperi*[1]; D. K. Matlock[1]; J. G. Speer[1]; [1]Colorado School of Mines, Advanced Steel Processing and Products Research Center, Golden, CO 80401

The effects of coating and post coating processing on the frictional behavior of two commercially produced hot dip galvanized interstitial free sheet steels were evaluated. Coatings were processed to minimize spangle size by control of bath chemistry (B material) and cooling rate (W material). For each coating method, samples were obtained in the as-coated, as-coated plus tension leveled conditions exhibited similar roughness values: 53 FM R_a and 81 PPI for the W material and 29 Fm R_a and 44 PPI for the B material. Temper rolling significantly increased the roughness of both materials and produced similar values of 68 Fm R_a and 154 PPI. The frictional behavior of the six experimental materials were determined with the bending under tension friction test at a displacement rate of 42.3 mm/s with a 25.4 mm diameter roller. With post-coating processing the W material exhibited a decrease in the coefficient of friction from the as-coated condition value of 0.16 to a low of 0.13 for the tension leveled. In contrast for the as-coated B material the friction coefficient was 0.12 and increased to 0.13 for both post processed materials. The extent of coating deformation and cracking on samples subjected to known strain histories (i.e. tensile strain with and without interfacial strain) were used as measurements of coating formability. The importance of the coating on overall sheet formability was evaluated with a friction model which incorporates surface microstructure and morphology, coating deformation and fracture behavior, and surface lubrication trapping characteristics.

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PRE-CRACKING AND CRACKING OF ZINC COATED STEEL SHEETS DURING DEFORMATION: *J. Lietzau*[1]; M. J. Philippe[1]; C. Esling[1]; J.Wégria[2]; M. Dubois[3]; [1]Metz Univeristy, LETAM, Metz France; [2]UM Research, Olen Belgium; [3]Cockress-Sambre, Flémalle Belgium

Five commercial galvanized steel sheets have been deformed by biaxial expansion. The microstructure of coatings, before and after deformation, has been studied using LOM, SEM, AND EBSP. Grain boundaries cracks are observed in each coating before deformation. After deformation, the cracks are enlarged and developed along the grain boundaries. Primary zinc dendrites as well as recrystallized grains can stop the cracks. After deformation, stone cleavage (intragranular fracture) is also observed.

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RESISTANCE WELDING ELECTRODE WEAR ON GALVANNEALED STEELS: *C. L. White*[1]; F. Lu[1]; M. Kimchi[2]; P. Dong[3]; [1]Michigan Technological University, Houghton, MI 49931; [2]Edison Welding Institute, Columbus, OH 43201-3693; [3]Battelle Memorial Institute, Columbus, OH 43201-2693

Resistance welding electrode wear on six different galvannealed steels has been evaluated using a standard constrant current electrode life tests. Metallographic aspects of the wear process have been characterized using light optical and scanning electron microscopy. Weld nugget evolution was also evaluated during the course of electrode life tests and correlated with electrode wear behavior. Galvannealed steels requiring the largest welding currents were observed to exhibit the lowest electrode lives. Coating substrate characteristics that influence welding currents and electrode life will be discussed.

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DISTRIBUTION OF ALUMINUM IN REGULAR HOT-DIP GALVANIZED STEEL COATINGS: *M. Gagné*[1]; S. Bélisle[1]; G. L. Espérance[2]; E. Boutin[2]; B Hong[2]; F. Goodwin[3]; [1]Noranda Technology Centre, Québec H9R 1G5 Canada; [2]Microscopique des Matériaux (CM), Centre de Caractérisation, Ecole Polytechnique, Montréal H3C 3A7 Canada; [3]Inernational Lead Zinc Research Organization, Research Triangle Park, NC 27709 USA

The final results from IIzro project ZCO 202 are presented in the paper. Selective wet chemical striping and electron beam metallographic techniques were evaluated and chosen for their ability to fully characterize the distribution of aluminum in regular hot dip galvanized steel coatings. Commercial samples were collected and examined to determine the effects of coating parameters on the distribution of aluminum in the coatings. Coating parameters investigated include steel type, line speed, strip temperature, bath temperature, bath aluminum level, and coating weight. Results of the chemical analyses and the metallographic examinations are presented. The results show that the line speed, bath aluminum level and coating weight impact on the aluminum distribution in the coating. Recommendations are made on processing conditions that lead to extremes in aluminum distribution in the coatings.

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PERFORMANCE EVALUATION OF PREPHOSPHATED ZETA-PHASE GALVANNEALED STEEL SHEET: *N. D. Kunde*[1]; G. M. Michal[1]; J. H. Payer[1]; [1]Case Western Reserve University, Department of Materials Science and Engineering, The Case School of Engineering, Cleveland, OH 41106-7204

Prephosphate treatments have been shown to improve the formability of galvannealed steel sheet processed to produce a surface comprised of delta-phase. At low phosphate coating weights of 0.5 to 1.5 g/m^2, this formability improvement occurs without any associated adverse effect on weldability. A program was undertaken to investigate the effect of low prephosphate coating weights on the forming, welding and adhesive bonding characteristics of galvannealed steel sheet processed to produce a surface comprised of zeta-phase. The effects of coating the untreated and prephosphated galvanneal with Quaker QVA 61 AUS mill were also examined. When galvannealed steel with a zetaphase surface was prephosphated with a trication phosphate coating weight of -1.5 g/m^2 a 14 percent reduction in cup test forming load was measured. The coefficient of friction determined by a draw bead simulator test was found to decrease by 14 percent for -0.5 g/m^2 prephosphate coating weight and by 21 percent for -1.5 g/m^2 prephosphate coating weight treatments. Also, a correlation between decreasing surface friction and increasing amounts of powdering was observed. Prephosphate treatments did not adversely affect the spot weldability, or change the adhesive bond strength of zeta-phase galvannealed steel.

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USE OF CUP TESTING TO ACCESS THE FORMING PROPERTIES OF PREPHOSPHATED GALVANNEALED STEEL SHEET: *N. D. Kunde*[1]; G. M. Michal[1]; J. H. Payer[1]; [1]Case Western Reserve University, Department of Materials Science and Engineering, The Case School of Engineering, Cleveland, OH 44106-7204

The application of a phosphate coating onto galvannealed steel strip has been shown to lower the coefficient of friction of its surface. Such prephosphate treatments cause an enhancement of the forming properties of the galvannealed steel strip. The correlation between the surface coefficient of friction and the deep drawing properties of galvannealed steel strip has been examined using cup tests. The tests have been performed such that measurements of the maximum load required to form a cup were made as a function of hold-down load. An equation that predicts the cup forming load as a function of the coefficient of friction, geometrical and flow properties of the test specimen has been used to isolate the effect of surface friction from the measured data. The surface coefficient of friction values determined through cup testing of prephosphated galvannealed steel samples were found to be in good agreement with values measured using draw bead simulator (DBS) friction tests. Predictions regarding the maximum increase in drawing ratio that can be achieved through prephosphate treatments of galvannealed steel will be discussed.

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STONE CHIPPING RESISTANCE AND COATING ROUGHNESS OF GALVANNEALED IF STEELS: J. Hammers[1], A. van der Heiden[1], W. van Koesveld[1], J.P. Schoen[1], Hoogovens Steel Strip Mill Products.

Abstract Not Available.

Extraction & Processing Division Luncheon

Speaker:
Charles O. Bounds
Rhone-Poulenc

Topic:
"The Rare Earths: Enablers for Modern Living"

Tuesday, February 17, 1998
12:00 noon

Location:
South Banquet Hall, Convention Center

1998 Extraction & Processing Distinguished Lecturer

Lecturer:
Michael J. Nicol
Murdoch University

Topic:
"Hydrometallurgy - The Crossroads of Science and Engineering"

Tuesday, February 17
1:45 p.m.
Location:
South Banquet Hall, Convention Center