TUESDAY AM

11TH INTERNATIONAL SYMPOSIUM ON EXPERIMENTAL METHODS FOR MICROGRAVITY MATERIALS SCIENCE: Session II

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

Program Organizer: R. A. Schiffman, R.S. Research, Inc., Crystal Lake, Barton, VT 05822 USA; C. Patuelli, Dipartimento di Fisica and Istituto Nazionale ci Fisica per la Materia, Alma Mater Studiorum, Berti Pichat 6/2, 40127 Bologna, Italy

Tuesday AM Room: 15B
March 2, 1999 Location: Convention Center

Session Chair: Carlo Patuelli, Instituto Nazionale ci Fisica per la Materia, Alma Mater Studiorum, Bolonga 40127 Italy

8:30 AM

WETTING BEHAVIOR OF BSO MELT ON PLATINUM: *Yu Zheng*[1]; A. F. Witt[1]; [1]Massachusetts Institute of Technology, 77 Massachusetts Ave., Cambridge, MA M.I.T. 13-4154 USA

Single crystal of Bi12SiO20 (BSO) is conventionally pulled from its melt by the Czochralski method [1-2]. To better understand the growth process and the mechanism of formation of defects, a Vertical Bridgman growth of BSO crystals under micro-gravity conditions has been proposed [3]. The crucible has to be made of Platinum, the only known material that is chemically stable when in contact with BSO melt. The interaction between BSO and Pt is extremely important when concern the thermal stresses caused by their different thermal expansion properties. In this work, the wetting behavior of BSO melt on platinum under an ambient with various partial pressure of oxygen is studied by the sessile drop method. The wetting angles as well as the surface tension of BSO melt are calculated by analyzing the shape of the sessile drops [4-5]. It is found that the BSO melt partially wets Pt at low pressure of oxygen ($\sim 10^{-4}$ atm) with an equilibrium contact angle around 45ϒ. The contact angle decreases as the pressure of oxygen goes up and approaches to zero when it is above 10-2 atm. The surface tension of BSO is about 200 mJ/m^2, which doesn't change with the pressure of oxygen. Finally, a design of the crucible for VB growth of BSO under micro-gravity conditions is given based on this wetting behavior. References: [1] O.F. Hill and J.C. Brice. The composition of crystal of bismuth silicon oxide. Journal of Materials Sciences, 9:1252, 1974. [2] C. Lin. Crystal growth and characterization of BSO. Doctoral Dissertation, Massachusetts Institute of Technology (1994) [3] A.F. Witt. Proposal on a Vertical Bridgman growth of BSO under Micro-gravity conditions [4] S. Harland and R. Hartley. Axisymmetric Fluid-Liquid Interfaces (Elsevier, Amsterdam, 1976) [5] S. Lahooti, O.I. Del Rio, A.W. Neumann, P.Cheng. Axisymmetric Drop Shape Analysis (ADSA). Applied Surface Thermodynamics (Marcel Dekker, Inc., New York, 1996), pp. 441

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DIRECTIONAL SOLIDIFICATION OF IMMISCIBLE 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, Mats. and Mech. Eng., Birmingham, AL 35294 USA; [2]NationalInstitute of Standards and Technology, Metall. Div., Gaithersburg, MD 20899 USA

Findings obtained from the Coupled Growth in Hypermonotectics experiment, which flew aboard the Life and Microgravity Spacelab mission, will be presented. During the mission, three immiscible Al-In samples were directionally solidified using the Advanced Gradient Heating Facility. These samples consisted of one 17.3wt% In monotectic composition sample and two hypermonotectic samples containing 18.5 and 19.7wt% In. All samples were initially heated to a temperature of 1100ϒ for 6 hours for homogenization and then directionally solidified at a rate of 1mm/s. X-ray analysis revealed that voids were present in some of these samples that could lead to local variations in thermal gradient and solidification rate. The microstructural variations in these samples will be reported and compared with the anticipated results from this experiment.

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STRIATION INDUCED BY UNSTEADY BRIDGMAN DIRECTIONAL SOLIDIFICATION: *R. Guerin*[1]; P. Haldenwang[2]; [1]Universite d'Aix-Marseille II, Laboratoire Matop, URA/CNRS 1530, Faculte des Sciences et Techniques de Saint-Jerome, Case 151, Marseille Cedex 20 F-13397 France; [2]Universite de Provence, IRPHE/UMR-CNRS 6594 IMT/Lajetee, Technopole de Chateau Gombert 38, Avenue Joliot-Curie, Marsceille Cedex 20 F-13451 France

Time-dependent behaviours induced by the solutal convection appearing above a solidification front are numerically investigated. The system under study corresponds to the upward Bridgman configuration for the directional solidification of the Pb-30%Ti alloy. The purpose of this work is to characterise the striations induced in the crystal when the flow becomes unsteady. We determine the onset threshold of unsteadiness as a function of confinement, and investigate the time behaviour of a given pattern versus the Rayleigh number for two different aspect ratios. More precisely, we estimate the magnitude of the time fluctuations in solute composition that the crystal incorporates. The period of the striations is also discussed. We indicate the flow conditions under which both quantities are appropriate for an experimental detection: a subcritical Hopf bifurcation is found more favourable for experimental observation of striation than a supercritical one. Unsteadiness in 3-D solutal convection is also considered.

9:30 AM

THE INFLUENCE OF G-JITTER ON PARTICLE INCORPORATION BY AN ADVANCING SOLID/LIQUID INTERFACE: *Carolyn L. Russell*[1]; Reginald W. Smith[1]; [1]Queen's University, Dept. of Mats. and Metall. Eng., Kingston K7L 3N6 Canada

It has been observed in transparent analogues of freezing metals, that particles existing in the melt may be pushed ahead of a macro-planar interface or occluded (captured) depending on whether the rate at which the solid/liquid interface is advancing is smaller or greater than some critical value (Vc). Various attempts have been made to provide a physical understanding of this. However, when experiment values for Vc are obtained they often differ widely from those predicted by the various models. In an attempt to simplify the experimental observations, a series of aluminum-based liquid metal matrix composites have been processed on the MIR Space Station. The samples were frozen unidirectionally using the gradient-freeze technique in the QUELD II furnace facility. This was attached to the Canadian Microgravity Isolation Mount (MIM). The MIM was used in three modes "Latched", "Isolating" and "Forcing". This permitted the influence of the fluid transport resulting from g-jitter, both "natural" and "forced", on the particle incorporation process to be determined. In addition, these experiments attempted to assess the influence of particle shape, thermal conductivity and volume fraction on Vc. The experiments and the results obtained will be presented.

9:50 AM BREAK

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ROTATING MOLTEN METALLIC DROPS AND THEIR APPLICATION TO SURFACE TENSION MEASUREMENT: *Won-Kyu Rhim*[1];

Takehiko Ishikawa[2]; [1]California Institute of Technology, Jet Propulsion Laboratory, 4800 Oak Grove Dr., Pasadena, CA 91109 USA; [2]Space Utilization Research Center, NASDA, (On leave from the Nationals Space Development Agency of Japan), 2-1-1 Sengen, Tsukuba, Ibaraki 305 Japan

Shapes and stability of rotating molten metal drops were experimentally investigated, and the feasibility of an alternative method for surface tension measurement was examined. Molten aluminum and tin drops approximately 3 mm in diameter were suspended in a high vacuum in a high temperature electrostatic levitator, and they were systematically rotated by applying a torque which was generated by a rotating magnetic field along the vertical axis. As the drop angular momentum was gradually (or step by step) increased from the static state, the drop shape evolved first along the axi-symmetric branch until the bifurcation point was reached at which transformation from axi-symmetric to triaxial shape took place With the assumption of 'effective surface tension' which includes the effect of reduced surface tension due to the surface charge, the results agreed quantitatively well with the Brown and Scriven's prediction. The normalized angular velocity at the bifurcation point agreed with the predicted value of 0.559 within 2%. Finally, an alternative surface tension measurement technique for high viscosity liquids, where the sample oscillation technique cannot be applied, will be presented.

10:30 AM

FINITE ELEMENT ANALYSES OF DROPLET DEFORMATION AND OSCILLATIONS IN MICROGRAVITY: Suping Song[1]; *Ben Q. Li*[1]; [1]Washington State University, School of Mech. and Mats. Eng., Pullman, WA 99163 USA

Finite element models are developed to represent the phenomena of surface deformation, oscillation, fluid flow and heat transfer associated with droplets positioned by either electrostatic or magnetic fields in microgravity. Numerical results are presented and compared with analytical or asymptotic solutions and/or experimental measurements that are available. The implications of results to the space measurements of thermophysical properties such as viscosity and surface tension are also discussed.

10:50 AM

DIFFUSION-LIMITED AND INTERFACE KINETIC-CONTROLLED CRYSTAL GROWTH IN SUCCINONITRILE AND PIVALIC ACID (PVA): *Afina Lupulescu*[1]; Martin E. Glicksman[1]; Mathew B. Koss[1]; Jeffrey C. Lacombe[1]; Laura T. Tennenhouse[1]; Julie E. Frei[1]; Douglas Corrigan[1]; [1]Rensselaer Polytechnic Institute, Dept. of Mats. Sci. and Eng., Troy, NY 12180 USA

Dendritic growth is generally considered to be kinetically controlled by a diffusion-limited process. The growth of dendrites in pure melts is controlled by the transport of latent heat from the moving boundary as it advances in supercooled melt. However, determining the interfacial speed at which attachment kinetics dominate the growth process and diffusion becomes relatively important, and remains uncertain except in broad theoretical terms. We focus here on experimental evidences of diffusional limited transport, and interfacial kinetic effects. The data will be presented for succinonitrile (BCC), and pivalic acid (FCC). The Isothermal Dendritic Growth Experiment (IDGE) is a basic science experiment designed to provide terrestrial and microgravity data which measure the kinetics, morphology, and dynamics of dendritic solidification under diffusion control. This experiment is a NASA-developed flight experiment and has already flown three times (USMP-2 and USMP-3 using SCN, and USMP-4 using PVA). USMP-2 and USMP-3 flight data, when compared to terrestrial dendritic growth data demonstrate that: 1) in the supercooling range from 0.47K to 2.1K microgravity data are free of growth chamber boundary and convective effects; b) these data may also be used to examine diffusion-limited, dendritic growth theories. Previous ground based experiments showed that the SCN dendritic growth is controlled by kinetic effects only at high supercoolings (higher than 5K). Trivedi & Mason (1991) claimed to show large kinetic effects in a PVA sample growing with a planar interface under steady-state conditions. The liquid-solid interface temperature, in their experiment, deviated substantially from the PVA melting temperature. The authors considered Ò highly nonlinear interface kinetic effects present during the solidification of PVAÓ. The IDGE results contrast with the results of Trivedi & Mason. USMP-4 microgravity data indicate that PVA dendritic growth is limited by diffusional transport. The effects of interface attachment kinetics are insignificant, even for the highest velocity observed (875 microns/sec).

11:10 AM

DIFFUSION EFFECTS ON LIQUID PHASE SINTERED Co-Cu SAMPLES IN MICROGRAVITY: *Y. He*[1]; J. Naser[1]; J. Chiang[1]; J. E. Smith[1]; [1]University of Alabama in Huntsville, Chemical and Mats. Eng., Huntsville, AL 35899 USA

This paper discusses the diffusion controlled grain growth of Co-Cu samples processed under microgravity. Twelve powder compact samples with solid volume fraction ranging from 50% to 70% were processed at 1473K during liquid phase sintering (LPS) experiments aboard sounding rockets and Space Shuttle missions. Processing time ranged from 2.5 to 66 minutes. The diffusional layer associated with processing time was observed and the experimental results on the grain size distribution and grain-coarsening rate are presented. The concentration distribution results based on SEM analysis are also presented. The diffusional effects on dihedral angle and particle sphericity are also discussed. The microstructural characterization revealed the agglomeration and coalescence occurred during liquid phase sintering of Co-Cu samples. The modified grain growth model that incorporates coalescence and particle sphericity (LSEM) appears to describe the observed grain growth behaviors far better than the LSW model.

11:30 AM

QUANTITATIVE COMPUTER TOMOGRAPHY FOR DETERMINING COMPOSITION OF MICROGRAVITY AND GROUND BASED SOLID SOLUTIONS: *D. C. Gillies*[1]; H. P. Engel[2]; [1]NASA/Marshall Space Flight Center, Huntsville, AL 35812; [2]*Wyle Laboratories, Kennedy Space Center, Cape Canaveral, FL 32899 USA

Advances in x-ray Computer Tomography (CT) have been led by the medical profession, and by evaluation of industrial products, particularly castings. Porosity can readily be determined as a function of the density of a material, and CT is thus an industrially important NDE tool. Providing high purity, 100% dense standards of pure elements and compounds can be fabricated, the composition of solid solution alloys can be determined by measuring the CT number, which is a function of the absorption of the sample. Average densities across slices 1 mm thick can generally be determined to better than 1 percent. With present technology this spatial sensitivity is less than ideal, but important benefits can nevertheless be obtained by using CT, particularly single crystals, prior to making any destructive assault upon the sample. The sample can in fact be examined prior to removal from the mold within which it has been grown and, in the cases of microgravity flight samples, before removal from the cartridge assembly. This greatly assists the researcher in the characterization of the products, particularly as a guide to cutting and sampling. Examples of work with germanium-silicon alloys and mercury cadmium telluride taken with a radioactive cobalt source will be demonstrated.

ALUMINA AND BAUXITE: Spent Bauxite Use and Processing

Sponsored by: Light Metals Division, Aluminum Committee
Program Organizer: Joe Anjier, Kaiser Aluminum & Chemical Corporation, P.O. Box 3370, Gramercy, LA 70052 USA

Tuesday AM Room: 6E
March 2, 1999 Location: Convention Center

Session Chair: Kenneth W. Ryan, ALCOA, Point Comfort Works, Point Comfort, TX USA

8:30 AM
DRY STACKING OF BAUXITE RESIDUE: *Fred S. Williams*[1]; Dana T. Smith[1]; [1]ALCOA, Point Comfort, TX USA

Dry stacking of bauxite residue has been shown to be an economical method for disposal compared to the wet lake disposal methods previously used in the alumina industry. A number of factors affect the slope which a bauxite residue will form in a stack deposit. Relationships useful for design and control of the slope of bauxite residue stacks will be discussed in this paper.

9:00 AM
TRACE ELEMENT PARTITIONING AND BIOAVAILABILITY IN RED MUD SYNTHETIC WETLAND SEDIMENT: *Gerald L. Goldstein*[1]; Robert S. Reimers[1]; David B. Kirkpatrick[2]; [1]Tulane University, Environmental Health Sciences, 1501 Canal St., New Orleans, LA 70112 USA; [2]Kaiser Aluminum and Chemical Corporation, Gramercy, LA USA

Over twenty-five square miles of Louisiana wetlands are lost per year due to coastal erosion and sediment starvation. A sediment source is needed for replenishment of the marshes, and dredged sediment is often polluted and unsuitable for placement in the wetlands. Consequently, it has been proposed that spent bauxite be used as an alternative to natural sediment. However, prior to use, it is important to evaluate the potential environmental impact of red mud in the wetlands. Specifically, the fate of red mud trace metals and the potential toxicity of red mud amended sediments to aquatic organisms need definition. Tulane University, in conjunction with Kaiser Aluminum & Chemical Corp., investigated the binding, partitioning, and bioavailability of key trace metals in synthetic blends comprised of red mud and natural sediment. Heavy metal behavior in red mud/sediment blends was studied using extraction, adsorption and bioaccumulation experiments. The results form these experiments are discussed herein.

9:30 AM
RED MUD PRODUCT DEVELOPMENT: *Seymour O. Brown*[1]; David B. Kirkpatrick[1]; [1]Kaiser Aluminum & Chemical Corporation, P.O. Box 3370, Gramercy, LA 70052 USA

Kaiser Aluminum & Chemical Corporation has impounded spent bauxite behind levees for over 20 years. In 1994, Kaiser embarked on a project to de-water the mud lakes at its Gramercy Louisiana Plant and to develop beneficial uses for the reclaimed lands and processed red mud. The work was presented at the 1996 TMS Annual Meeting. Kaiser is continuing its research into red mud uses. Kaiser has developed methods to use this material to make levees. Kaiser and Colorado School of Mines have researched the extraction of other metals from the spent bauxite. Kaiser and Tulane University have researched the making of synthetic soils as well as the use of red mud as a sewerage disinfectant. The status of these projects will be discussed in this presentation.

10:00 AM BREAK

10:30 AM
WASTE FREE ALUMINA PRODUCTION FROM NON-BAUXITIC RAW MATERIALS: *G. Z. Nasyrov*[1]; V. V. Pivovarov[1]; S. Y. Dantzig[1]; V. A. Lipin[1]; [1]VAMI, 86 Sredny Pr, St. Petersburg 199026 Russia

From an ecological point of view, the best system to produce alumina results in the production of no waste streams. This can be accomplished when processing non-bauxite materials. The joint treatment of nepheline and alunite ores to produce alumina, potassium sulfate, cement, light weight aggregates and other materials is such a process. This paper covers the potential of utilzing alkaline alumosilicate and alunite raw material and the economics of these processes. Some flowsheets of alunite and alumosilicate processing and the techno-economic parameters of complete treatment are shown.

11:00 AM
UTILIZING ALUMINA PLANT WATER DISCHARGE STREAMS: *Gan GuoYao*[1]; Wang Longzhang[1]; [1]Pingguo Alumina Plant, Pingguo, Guangxi China

A new technology of making use of the Contaminated water produced in the Pingguo Alumina plant was developed. After treating the water in a processing center, the contaminated water is used to cool precipitators and to clean the boiler smoke generated by the combustion of coal. By developing this technology, the productivity of the plant was increased by 5%, and the rates of removing sulfur dioxide and dust from the boiler smoke by 35%. This new technology gives good results, is economical and protects the environment.

ALUMINUM REDUCTION TECHNOLOGY: Environmental

Sponsored by: Light Metals Division, Aluminum Committee
Program Organizers: Georges J. Kipouros, Dal Tech, Dalhousie University, NS B3J2X4 Canada; Mark P. Taylor, Comalco Aluminium, Ltd., Brisbane, Queensland 4001 Australia

Tuesday AM Room: 6F
March 2, 1999 Location: Convention Center

Session Chair: Reidar Huglen, Hydro Aluminium Karmoy Metallverk, Havik N-4265 Norway

8:30 AM
THE ELECTRODE KINETICS OF PERFLUOROCARBON (PFC) GENERATION: *D. R. Sadoway*[1]; *H. Zhu*[1]; [1]Massachusetts Institute of Technology, Dept. of Mats. Sci. and Eng., 77 Massachusetts Ave., Room 8-109, Cambridge, MA 02139-4307 USA

The generation of CF_4 and C_2F_6 is being studied in a laboratory-scale aluminum reduction cell. During electrolysis in well behaved cells and in cells on anode effect, anode gases have been analyzed by gas chromatography on-line. Electroanalytical techniques such as ac voltammetry and electrochemical impedance spectroscopy are being used to determine the values of the kinetic parameters associated with the electrochemical reactions occurring on the anode as a function of various operating conditions, e.g., anode composition, bath chemistry, and temperature. The research is sponsored jointly by the Aluminum Association and the U.S. Environmental Protection Agency.

9:05 AM
SPECTRUM ANALYSIS OF THE BUBBLING ACOUSTIC SIGNALS THROUGH CARBON ANODES: *Jilai Xue*[1]; Harald A. Øye[2]; [1]SINTEF Applied Chemistry, Trondheim N-7034 Norway; [2]Norwegian University of Science and Technology, Institute of Inorganic Chemistry, Trondheim N-7034 Norway

The information on anode bubbling is important for cell operation and new cell design. However, it is extremely difficult to have direct observation on the bubbling process during cell operation due to the high temperature and corrosive conditions. This paper will present an alternative approach to investigate the in situ bubbling behavior by detecting the sound signals from the anodes. The correlation between the sound signals and the anode bubbling was observed in both water modeling and industrial tests. A portable computer system with on-line data acquisition and spectrum analysis functions has been developed for use in industrial environment. The signal patterns on normal anodes in a cell were obtained as reference. The variation in signal pattern with anode spike was investigated.

9:35 AM
POT GAS FUME AS A SOURCE OF HF EMISSION FROM ALUMINIUM SMELTERS - LABORATORY AND FIELD INVESTIGATIONS: *A. B. Heiberg*[1]; G. Wedde[1]; [1]ABB Miljø AS, P.O. Box 6260 Etterstad, Oslo N-0603 Norway

HF measurements carried out in treated pot gas from aluminium smelters equipped with dry scrubbing occasionally show higher emission levels than expected from current HF penetration-saturation relationships. The excess HF emission might be caused by a chemical reaction between particulate fluoride compounds (fume particles) originating in the electrolytic bath and moisture present in the pot gas. To test this hypothesis samples of dust collected at an aluminium smelter were ex-

posed to hot, humid air in the laboratory. The HF concentration was measured in the exit gas at frequent intervals over a time period of several hours. Both "pure" fume, and mixtures of fume and alumina identical to the dust that is constantly added to the filter bags used in the scrubbers, were investigated. Samples of exposed filter bags were also tested. With gas temperature and humidity kept at the relevant levels a noticeable emission of HF is observed both from dust and filter, confirming that particulate fluorides may be a significant source of HF in the clean gas. Mathematical models quantifying the relation between HF concentration and temperature, humidity and F-content in the dust were developed and applied to data collected at a smelter in the Middle East. The plant simulations indicate that reactive fume may account for about one third of total dry scrubber HF emissions. Both the fume-related and the total emission is significantly affected by temperature. Means to minimize the contribution from the fume are suggested.

10:00 AM BREAK

10:30 AM
VENTILATION OF POTROOMS IN ALUMINIUM PRODUCTION: *N. J. Holt*[1]; N. M. Anderson[2]; M. Karlsen[1]; T. Foosnaes[1]; [1]Hydro Aluminium AS, Technology Centre Ardal, P.O. Box 303, Ovre Ardal N-5870 Norway; [2]Hydro Research Centre, P.O. Box 2560, Prosgrunn 3901 Norway

Potrooms for the production of aluminium are preferably naturally ventilated. Air flow rates may vary from 8-24 Nm^3/s/pot, depending on cell technology, building layout and location. As focus on environmental issues increases, it becomes also more important to control the ventilation so that the best possible working atmosphere may be achieved. This paper concentrates on the main parameters which must be kept under control, and which may be used to control the ventilation, e.g. the design of the cellar, the use of wind shields and the area and position of the floor gratings. We also present measurements and numerical simulations to illustrate how existing potroom buildings may be converted from mechanical to natural ventilation. It is further important to realize that climatic conditions should be considered and that these may vary significantly among places where aluminium smelters are located. Locations with tropical climates with average temperatures well above 30ϒC and often high air humidity, thus represent a different challenge with respect to ventilation when compared to a smelter located in a temperate climate.

11:00 AM
TREATMENT AND REUSE OF SPENT POT LINING, AN INDUSTRIAL APPLICATION IN A CEMENT KILN: *P. B. Personnet*[1]; [1]Aluminium Pechiney, LRF BP114, 73303 Saint Jean De Maurienne, Cedex France

The treatment of Spent Pot Lining (SPL) has been the occasion of numerous studies in the world. Several processes have reached the commercial stage in USA, Australia and Europe. Most of these processes generate waste that need to be disposed of. Another approach is to make total use of the SPL constituents, with no waste disposal and with no air emission. Among several processes allowing reuse of SPL, one is highlighted here: the addition of second cut (refractory) SPL to quarry materials in the raw feed of a Cement Kiln. Under close supervision of the French Environment Protection Authority, ALUMINIUM PECHINEY has developed a partnership with CIMENTS D'ORIGNY including an R&D programme to demonstrate the capability of a Cement Kiln to accept SPL as a raw material despite the presence of sodium and fluoride. Since 1997, SPL is now recycled industrially in a Cement Plant of Northern France.

ANALYTICAL TECHNOLOGY IN THE MINERAL INDUSTRIES: Instrumental Analytical Methods in Mineral Processing

Sponsored by: Extraction & Processing Division, Process Mineralogy Committee; ASTM Subcommittee E01.02
Program Organizers: Louis J. Cabri, CANMET, Ottawa, Ontario K1A 0G1 Canada; Charles H. Bucknam, Newmont Metallurgical Services, Englewood, CO 80112 USA; Steven L. Chryssoulis, Amtel, London, Ontario N6G 4X8 Canada; Rebecca A. Miller, Minekeepers, Phoenix, AZ 85014 USA; Emil Milosavljevic, Lakewood, CO 80227 USA

Tuesday AM Room: 7A
March 2, 1999 Location: Convention Center

Session Chairs: Emil B Milosavljevic, Lakewood, CO 80227 USA; Charles H. Bucknam, Newmont Technical Facility, Newmont Metallurgical Services, Englewood, CO 80112 USA

8:30 AM INTRODUCTION TO SESSION

8:35 AM INVITED PAPER
EVALUATION OF ICP-MS AND GF-AAS METHODS FOR ANTIMONY DETERMINATION IN GROUNDWATERS: *Rahul S. Bhaduri*[1]; Lucinda Tear[2]; [1]Newmont Gold Company, Twin Creeks Mine, P.O. Drawer 69, Golconda, NV 89414 USA; [2]Parametrix, Inc. USA

The EPA promulgation of the Safe Drinking Water Act (SDWA) requires that the Maximum Contaminant Level (MCL) for antimony in ground waters not exceed 6 ppb. The selected analytical method(s) should reliably quantify antimony near the MCL. This paper presents an interpretation of analytical results from extensive bench and pilot scale investigations geared towards removing antimony to below the MCL in treated ground water. Filtered head and effluent sample splits, from daily runs, were sent to five State certified laboratories for a total period of 25 days; two facilities employed Graphite Furnace-Atomic Absorption Spectrometry (GF-AAS), two others used Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) and a fifth adopted both methods. Scatter plots, for individual laboratories, were used to visually assess the type of relationships that existed between residual antimony and independent process variables. As the relationships were linear, the Pearson correlation coefficient was used to estimate the strength and significance of the dependency. The correlation between process variables and residual antimony concentrations were more significant, and varied less between laboratories, when the ICP-MS method was employed. The findings indicate that ICP-MS is a more precise analytical instrument for determining low levels of antimony in treated groundwater.

9:00 AM INVITED PAPER
APPLICATION OF ICP-MS IN SOLVING PRACTICAL ANALYTICAL PROBLEMS IN MINE MATERIALS: *Dana Mills*[1]; Hugh deSouza[1]; Paul Burgener[1]; [1]X-Ray Assay Laboratories, 1885 Leslie St., Ontario M3B 3J4 Canada

ICP-MS has moved from a laboratory curiosity to a functional analytical tool. This paper will discuss how ICP-MS has been used to solve difficult analytical procedures in analyzing mine materials. Comparisons between analytical techniques applied to the analysis of gold and the platinum group metals will illustrate the advantages and problems of ICPMS when applied to trace levels of some metals in the presence of ore grade metals. Interferences and matrix effects are compared to ICP, AA and Neutron Activation. The necessity of selecting chemical extractions which are compatible with ICPMS are also discussed. The ICPMS techniques explained in the examples on Au and PGE's have validity in analytical problems encountered in testing of trace metals in the presence of major elements found in mine materials. Exploration

and environmental testing are other areas which require the same analytical approach to quantify trace levels in the presence of major interfering elements normally associated with mining environments.

9:25 AM INVITED PAPER

ANALYTICAL TECHNIQUES USED FOR THE RECYCLING OF LEAD FROM FIRE ASSAY WASTES: *Carl C. Nesbitt*[1]; Sui Xue[2]; [1]Michigan Technological University, Dept. of Metall. and Mats. Eng., 1400 Townsend Dr., Houghton, MI 49931 USA; [2]Eichrom Industries, Inc., 8205 S. Cass Ave., Suite 107, Darien, IL 60561 USA

A project has been completed which investigated the efficacy of recycling lead or lead monoxide from various fire assay wastes, including crucibles, cupels and slag. The scope of the project was to determine if hydrometallurgical treatment of the materials could be optimized so that direct separation and recovery of lead salts was economically feasible. A process was developed from the study which could use either acetic acid or nitric acid as a leachant, followed by several precipitation processes which could directly recover litharge (PbO) or other lead salts, such as lead carbonate or lead sulfate. Analytical equipment such as the atomic absorption spectrophotometer and x-ray diffractometer supplied much of the information required. However, some novel analytical approaches using these instruments had to be developed to help in the determination of leaching kinetics and process quality control. These techniques will be presented.

9:50 AM INVITED PAPER

CHARACTERIZATION AND STABILITY OF ARSENITE AND ARSENATE IN THE IRON-ARSENIC AND LANTHANUM-ARSENIC SYSTEMS: *M. Misra*[1]; A. Rawat[1]; J. Nanor[1]; [1]University of Nevada, Reno, Chem. and Metall. Eng., Mackay School of Mines, MS 170, Reno, NV 89557 USA

The precipitation vs adsorption of arsenite and arsenate species onto iron and lanthanum compounds has been discussed. Several analytical and characterization techniques such as XRD, FTIR, Zeta Potential and AFM have been used to establish the nature of bonding. An advanced CHEMDRAW computer program has been used to estimate the bond strength and nature of adsorption.

10:15 AM BREAK

10:45 AM INVITED PAPER

COMBINING FTIR SPECTROSCOPY AND MULTIVARIATE CALIBRATION TO LOCATE MINERABLE ORE DEPOSITS: *Sharon L. Eyer*[1]; [1]Alcoa of Australia, Ltd., Research and Development Dept., P.O. Box 161, Kwinana 6167 Western Australia

FTIR spectroscopy can be a used to estimate the quality of an ore body based on exploration samples. Furthermore it can highlight regions of ore that are relatively unusual. Unusual ore can be investigated for potential impacts on refinery processes well in advance of mining. The technology has been successfully implemented at an alumina refinery in Kwinana, Australia, for assessment of ore attributes such as available alumina, extractable organic carbon and total iron. Classical methods of analyses for these properties involve laboratory-scale digestion of alumina ore (bauxite) or XRF analyses. Multivariate calibration is used to generate robust models that are able to estimate classical data from FTIR spectral data. The latter are collected from powdered bauxite at a throughput of less than a minute per sample. The technique is illustrated conceptually and an example application for bauxite is presented. Challenges and difficulties are discussed. The potential to expand the technique to process control is introduced.

11:10 AM INVITED PAPER

IN-SITU FT-IR/IRS AND MLRS EXAMINATION OF OLEATE ADSORPTION AT FLUORITE AND CALCITE SURFACES: *Courtney A. Young*[1]; J. D. Miller[2]; [1]Montana Tech of the University of Montana, Dept. of Metall. Eng., Butte, MT 59701 USA; [2]University of Utah, Dept. of Metall. Eng., Salt Lake City, UT 84112 USA

Adsorption isotherms previously determined by in-situ Fourier transform infrared/internal reflection spectroscopy (FT-IR/IRS) for oleate adsorbed at calcite and fluorite surfaces near pH 9 and at various temperatures are compared. Results indicate that, at both mineral surfaces, chemisorption occurs at equilibrium concentrations below approximately $1x10^{-5}$ M oleate while calcium dioleate surface precipitation occurs at higher equilibrium oleate concentrations. The extent of chemisorption at the calcite surface is 3 to 5 times less than that at the fluorite surface while the extent of calcium dioleate surface precipitation on calcite is nearly a magnitude larger than that on fluorite. However, for both minerals, surface precipitation decreases with increasing chemisorption. Contact angle measurements and flotation recoveries show that the hydrophobicity of fluorite to be greater than calcite at each of the temperatures and oleate concentrations studied. Significant differences are noted only in the chemisorption region. Unlike calcite, the hydrophobicity of fluorite was sensitive to the presence of oxygen in the system. Multichannel Laser Raman Spectroscopy (MLRS) showed this behavior was caused by the double-bond reactivity of adjacent chemisorbed oleate molecules and subsequent formation of an epoxide/polyether complex at the fluorite surface. Such a reaction product could not be detected at the calcite surface. These differences in adsorption density, hydrophobicity, and polymerization behavior are discussed in terms of the intrinsic surface properties of the minerals.

11:35 AM

CAN WE CLOSE THE "CYANIDE CYCLE"?: *Emil B. Milosavljevic*[1]; Ljiljana Solujic[2]; 8143 W. Eastman Place, #14-201, Lakewood, CO 80227 USA; [2]University of Nevada, Reno, Dept. of Chem., MS216, Reno, NV 89557 USA

Cyanide is exceptionally reactive, and in typical gold/silver processing liquors, cyanide may be transformed into various species and forms depending on the mineralogy of the ore and chemical make-up of the process water. The exact speciation and relative concentrations depend on the Eh and pH values, as well as the free CN^- concentration in the system. Very good cyanide balances can be achieved by the judicious selection of the analytical techniques used. The choices an analyst has to make (which analytical methods to use and which ones to avoid) in order to gain better understanding of cyanide speciation and balances in a particular system under investigation will be discussed. Examples of cyanide balances obtained for the laboratory scale tests (agitated leach and column tests) will be presented and discussed.

AUTOMOTIVE ALLOYS III: Session III — Developmental Studies

Sponsored by: Light Metals Division, Aluminum Committee
Program Organizer: Subodh Das, ARCO Aluminum Company, P.O. Box 32860, Louisville, KY 40232 USA

Tuesday AM Room: 3
March 2, 1999 Location: Convention Center

Session Chairs: Subodh K. Das, ARCO Aluminum, Inc., Louisville, KY 40232 USA; J. D. Bryant, Reynolds Metal Company, Chester, VA 23836-3122 USA

8:30 AM

PREDICTION OF YIELD STRENGTH OF THE PAINTED ALUMINUM AA6111 PANEL: *A. K. Gupta*[1]; [1]Alcan International, Kingston Research and Development Center, P.O. Box 8400, Kingston, Ontario K7L 5L9 Canada

The knowledge of the strength of the final part at the design stage is an important parameter in determining the optimum sheet gauge for maximum weight savings without sacrificing the desired dent resistance. The AA6111 sheet materials is relatively soft in the forming temper and becomes stronger from combination of work and age hardening during forming and paint cure operations, respectively. Presently, the strength of the painted part is determined from over-simplified experiments simulating the forming and paint cure processes. In this paper, the hardening model of AA6111 alloy is used to predict the strength following multiple step ageing, both with and without prestrains. The

approach developed in the paper is used to predict the strengths that are obtained from the simulation experiments and comparisons are made with the strength and dent data measured from different locations of an actual painted part.

8:50 AM

OPTIMIZED 6XXX ALUMINUM ALLOY SHEET FOR AUTOBODY OUTER PANELS: *Ravi A. Shahani*[1]; Dominique Daniel[1]; [1]Pechiney, Centre de Recherches de Voreppe, Centr'Alp, BP 27, 38340 Voreppe, Isere France

AA6016 is the aluminum alloy typically specified in Europe for autobody outer panels. Compared with the copper-rich alloys 6111, 6009 and 6010 often used in the US, 6016 shows better formability in the T4 condition but lower strength after the final bake-hardening treatment. As a result of the current trend towards lower paint-bake curing temperatures, a higher strength material than standard 6016 will be preferable for some applications in order to maximize the weight reduction offered by aluminum body panels while maintaining equivalent dent resistance to the steel alternative. This paper describes Pechiney's development programme for an alloy giving higher strength after bake-hardening than 6016, but with improved formability in stamping and hem flanging operations compared with current high strength aluminum automotive sheet alloys.

9:10 AM

MICROCHEMISTRY AND MICROSTRUCTURAL ASPECTS LEADING TO STRESS CORROSION CRACKING IN AA5083: *John S. Vetrano*[1]; M. J. Danielson[1]; D. R. Baer[1]; R. H. Jones[1]; [1]Pacific Northwest National Laboratory, P.O. Box 999, Richland, WA 99352 USA

The addition of Mg to Al increases its formability and strength, but at levels greater than about 3.5 wt.% it can increase the susceptibility to stress corrosion cracking (SCC) in salt water when exposed to moderate temperatures for long times. This precludes the use of high-Mg aluminum alloys for automotive use in load-bearing components. Careful measurements of grain boundary structure and composition in a commercial Al-Mg alloy (5083) have been carried out as a function of annealing time at 175ŸC using high-spatial resolution analytical electron microscopy in conjunction with Auger electron spectroscopy (AES). These results were compared to U-bend specimens heat-treated under the same conditions and exposed to an alternate immersion test in a 3.5% NaCl solution. It was found that the precipitation of the b-phase (Al3Mg2) was a necessary, but not sufficient, pre-requisite for SCC susceptibility. It was noted that specimens that were susceptible had a pronounced depletion of Mg at most grain boundaries between the b-phase particles. Pre-notched compact tension samples were then tested in a 3.5% NaCl solution under increasing loads until a crack was propagated. These measurements confirmed the susceptibility of the different conditions as found in the U-bend tests. The impact of these results on the understanding of the SCC mechanisms in Al-Mg alloys will be discussed and possible mitigation methods will be proposed.

9:30 AM

HOT DUCTILITY OF 6XXX ALUMINUM ALLOY FOR AUTOMOTIVE BODY SHEET: *Tsutomu Itou*[1]; Masayuki Ishikawa[1]; Masahisa Otsuka[1]; Makoto Saga[2]; Masao Kikuchi[2]; [1]Shibaura Institute of Technology, Dept. of Mats. Sci. and Eng., 3-9-14, Shibaura, Minato-Ku, Tokyo 1088548 Japan; [2]Nippon Steel Corporation, Shintomi-cho, 20-1, Futtsu, Chiba 2930011 Japan

Recently 6XXX aluminum alloys have begun to be used for both automotive body sheet panel and space frame in order for weight saving. However, their application is limited to sports cars or high-glade cars. This is partially caused by the lack of plastic workability in these alloys, though both specific stiffness and strength are sufficiently high. In particular, maintaining the hot workability seems to be essential for the substitution of steel sheet with aluminum one. In this paper, the high temperature characteristics of two kinds of 6XXX alloy rolled sheets in T4 condition have been investigated with special reference to the applicability of superplastic forming. Constant cross head speed tensile tests are conducted at various temperature and strain rate ranging, respectively, from 623 to 803K and from 3x10-5 to 1x10-1s-1. Both at 773K and at 803K the total elongation vs. strain rate diagram has a minimum of 160% near the strain rate about 1x10-3s-1. It is to be noted that the typical fracture mode changes from intergranular type in lower strain rate range to transgranular one in higher strain rate range. Total elongation increases rapidly with decrease in strain rate resulting in superplastic-like ductility more than 300%. The deformation mechanism is discussed on the basis of microstructural observation. The mechanical anisotropy will also be described briefly.

9:45 AM

AUTOMOTIVE ALLOYS: *D. J. Lloyd*[1]; [1]Alcan International, Ltd., Kingston Research and Development Center, P.O. Box 8400, 945 Princess St., Kingston, Ontario K7L 5L9 Canada

The ability to form the 6000 series Al alloys into complex shapes is important for the application of these alloys as automotive skin sheet. The alloys therefore require a level of ductility and bendability to achieve the degree of forming required. In this paper the work hardening, tensile ductility and bendability of several 6000 series alloys are examined. It is shown that the tensile ductility is predominantly controlled by the work hardening behavior, which subsequently controls geometrical instability and tensile failure. However, the bendability of the alloys is fracture controlled, and is essentially independent of tensile elongation. The bendability of the different alloys can be understood on the basis of fracture controlled models and the different fracture strains of the alloys. An approximate equation, developed previously primarily for steels, provides an adequate description of the minimum radius achieved in bending.

10:00 AM BREAK

10:30 AM

THE EFFECT OF PRE-AGING ON ARTIFICIAL AGING RESPONSE IN Al-Mg-Si-Cu ALLOY 6111: *Weifang Miao*[1]; David E. Laughlin[1]; [1]Carnegie Mellon University, Dept. of Mats. Sci. and Eng., 5000 Forbes Ave., Pittsburgh, PA 15213 USA

Although heat treatable Al-Mg-Si-Cu alloys are increasingly used as automotive body materials, the potential of these alloys is not fully utilized due to low temperature and short duration of the automotive paint bake cycle, during which the alloys are artificially age hardened after stamping. Moreover, practically unavoidable natural aging process is usually detrimental to the artificial aging response of these alloys. In this study, the effect of various pre-aging treatments on the artificial aging response of an aluminum alloy 6111 was investigated using hardness measurements, differential scanning calorimetry and transmission electron microscopy. It has been found that appropriate pre-aging treatments slow down the natural aging process and significantly increase the artificial aging response. The changes in artificial aging response are closely related to the variations in size and distribution of precipitates. Financial support from Ford Motor Company and NEDO is gratefully acknowledged.

10:45 AM

EFFECT OF ALLOY COMPOSITION AND PROCESSING ON THE FORMABILITY OF ALLOYS BASED ON Al-3 WT.% Mg: *S. A. Court*[1]; [1]Alcan International, Ltd., Banbury Laboratory, Southam Rd., Banbury, Oxon OX16 7SP England

Aluminum alloys in sheet form based on Al-3 wt.%Mg(AA5754and AA5454) have found application in automotive structures as they offer attractive combination of strength, formability, corrosion resistance and weldability. However, to allow down-gauging there is a continued need for 5xxx series alloys with increased strength as compared with the existing alloys, which must be achieved without adversely affecting other sheet properties. In this paper, the results of studies aimed at understanding the effects of both alloy composition and sheet processing on the strength and formability, in particular, of alloys based on Al-3 wt%Mg, are described.

11:00 AM

INVESTIGATION OF PROCESSING-MICROSTRUCTURE-PROPERTY RELATIONSHIPS IN Al-Mg-Mn ALLOYS: *Mark C. Carroll*[1]; Jörg M. K. Wiezorek[2]; Michael J. Mills[1]; *Glenn S. Daehn*[1]; Brady R. Dunbar[3]; K. Paul Smith[3]; [1]Ohio State University, Dept. of Mats. Sci. & Eng., 2041 College Rd., Columbus, OH 43210 USA; [2]Uni-

versity of Pittsburgh, Dept. of Mats. Sci. and Eng., University Way, Pittsburgh, PA 15261 USA; [3]Century Aluminum Corporation, Ravenswood Operations, Ravenswood, WV 26164 USA

The ever-increasing demand for high-strength, low-cost materials in various applications has necessitated the development of premium quality Al-Mg-Mn (5000 Series) alloys. Progress has been made in processing which can produce alloys with an optimum combination of dispersion and precipitation hardening, solid-solution strengthening, and fine grain sizes. Some of the optimum characteristics of these alloys, however, are subject to the deleterious effects of grain growth and Mg diffusion, leading to the formation of the Mg-based beta-phase along grain boundaries. Together with a decrease in strength of the alloy due to the loss of the Mg solid-solution strengthening, there is also concern over the alloys susceptibility to stress corrosion due to the galvanic reaction between the Mg-enriched areas and the Al matrix. The present work investigates strength and corrosion characteristics of Al-Mg-Mn alloys, with a focus on derivatives of AA5083. Observations have been made which correlate microstructure with mechanical strength and corrosion resistance in relation to established AA5083 baseline properties. Microstructural characterization by optical microscopy and analytical techniques of transmission electron microscopy (TEM) has been combined with physical testing, which includes hardness and exfoliation tests. The local microchemistries at grain boundaries and in the vicinity of inhomogeneities, as well as the identity of various types of dispersoid and precipitate phases, have been determined by energy dispersive X-ray spectroscopy and diffraction techniques using a state-of-the-art field-emission CM300FEG TEM. The microstructural observations are correlated to the macroscopic property measurements. For example, the tendency of such alloying elements as Zn to preferentially diffuse to grain boundaries and limit the diffusion of Mg is demonstrated. On the basis of observations and experimental results, the performance of Al-Mg-Mn alloys with regard to microstructural characteristics is discussed. Financial and technical support by Century Aluminum Corporation, Ravenswood Operations, is acknowledged.

11:15 AM

A SMALL-CRACK FRACTURE MECHANICS-BASED MODEL FOR PREDICTING THE S-N RESPONSE OF CAST ALUMINUM ALLOYS: *Michael J. Caton*[1]; J. Wayne Jones[1]; John E. Allison[2]; [1]University of Michigan, Mats. Sci. and Eng., 2300 Hayward, Ann Arbor, MI 48109-2136 USA; [2]Ford Motor Company, Mats. Sci. Dept. - Research Staff, MD 3182 Scientific Research Lab, 20000 Rotunda, Dearborn, MI 48121 USA

With increased use of cast aluminum alloys in demanding automotive applications, there exists a need for a reliable method to accurately predict an alloy's fatigue properties. It has been speculated that the fatigue properties of aluminum castings are dominated by the propagation of cracks which initiate from shrinkage pores ranging in size from ~ 50 to 500 µm. With this in mind, the growth of small fatigue cracks (~15µm to 2 mm) was monitored in a 319-type aluminum, a common Al-Si-Cu alloy used in casting engine blocks and cylinder heads. A plot of the growth rates as a function of the stress intensity factor range, ΔK, indicates the existence of a small crack effect as well as a significant influence of the solidification rate and applied stress level on the resulting da/dN vs. ΔK curves. A crack growth relation proposed by Nisitani and others is modified and used to correlate the small crack data. Predictions of the S-N response based on this small crack model and based on a Paris relation for long crack data are compared to experimental S-N data.

11:30 AM

AGE HARDENING BEHAVIOR IN A COMMERCIAL 319-TYPE ALUMINUM ALLOY: *Ray Jahn*[1]; William T. Donlon[1]; John E. Allison[1]; [1]Ford Motor Company, Ford Research Laboratories, P.O. Box 2053, MD 3135, Dearborn, MI 48121 USA

Cast Al-Si-Cu alloys are utilized by the automotive industry for engine blocks and cylinder heads. Detailed understanding of the ageing characteristics of these types of alloys is important to optimize the processing of these components to yield the desired physical and mechanical properties. Age hardening curves for temperatures between 100 and 305°C have been determined after a solution treatment at 495ϒC for 8 hours for a commercial grade 319-type Al alloy (7.08wt% Si, 3.26%Cu, 0.16%Mg, 0.23%Mn, 0.4%max Fe, 0.25%max Zn, 0.25%max Ti). The influence of casting solidification rate on the subsequent ageing response was characterized by measuring the hardening curves in samples solidified at 2.38ϒC/sec (SDAS=30ÿm) and 0.033°C/sec (SDAS=110ÿm). The phases formed within the primary aluminum dendrites during each stage of age hardening were characterized using a JEOL 2000FX TEM and an OXFORD ISIS microanalysis system. The initial stage of hardening at 100 and 150°C is believed to be due to clustering of Cu atoms, followed by the formation of GP zones. At longer times and higher temperatures small (5nm) lath-shaped Q (Al5Mg8Si6Cu2) precipitates and disk-shaped ÿ‘ precipitates occur at peak hardness and coarsen during overaging. The observed orientation relationship for ÿ‘-Al is [100]ÿ‘ // [100]Al and [001]ÿ‘ // [001]Al, and that for Q-Al [0001]Q // [001]Al and (1120)Q // (310)Al, consistent with the literature results. Coprecipitation of Q and ÿ‘ phases were found in as-cast material with an approximate orientation relationship [0001]Q // [100]ÿ‘ // [100]Al. The size, spacing and density of ÿ‘ precipitates have been determined as a function of ageing temperature and time.

11:45 AM

A PROCESS MODEL FOR THE AGE HARDENING OF A 319-TYPE ALUMINUM ALLOYS: *P. M. Reeber*[1]; [1]University of Michigan, Dept. of Mats. Sci. & Eng., Ann Arbor, MI USA

The age hardening response of a 319-type aluminum alloy was studied by examining the variation of yield strength and proportional limit with aging time and temperature. Aging curves were constructed for cast materials produced by two different solidification rates. Aging temperatures ranged from 130-305ϒC for periods up to 1000 hours. The aging curves follow conventional diffusion controlled precipitation hardening behavior. Using this data, a process model was developed that is based on an approach suggested by Shercliff and Ashby [H. R. Shercliff and M. F. Ashby, Acta metall. mater. 38, 1789 (1990)]. The process model predicts the changes in yield strength and proportional limit that result from isothermal aging. The components of the model are outlined, and the deviation of measured behavior from that predicted by the modified Shercliff-Ashby model is discussed for both solidification rates. The results show that the aging process of 319 Al can be reasonably predicted by the age-hardening process model. A variant of the model describing the effects of thermal exposure on aging behavior will also be discussed.

CARBON TECHNOLOGY: Anode Plant Retrofitting & Operation

Sponsored by: Light Metals Division, Aluminum Committee
Program Organizer: C. Dreyer, Aluminium Pechiney, St Jean De Maurienne 73303 France

Tuesday AM — Room: 6D
March 2, 1999 — Location: Convention Center

Session Chair: Doug Parrish, Tomago Aluminium, Raymond Terrace, NSW, 2324, Australia

8:30 AM SESSION CHAIRMAN INTRODUCTION

8:35 AM

ADVANCES IN FORMING: Werner K. Fischer[1]; *Markus W. Meier*[1]; [1]R&D Carbon, Ltd., P.O. Box 362, Sierre CH-3960 Switzerland

Anodes of any size can be vibrated or pressed. Various reasons have led to the introduction of vibrators in the late seventies, mainly: - Increasing anode size - Higher investment cost for large presses - Pressing capacity limited by the mixing throughput - Unsatisfactory paste cooling. These reasons have become irrelevant due to the technical development in the recent years. Presses actually have some distinct advantages compared to vibrators: lower investment cost for anode

cooling, lower maintenance, higher availability, lower noise level and lower PAH emissions. The resulting anode quality is similar for both pressed and vibrated anodes. It is therefore believed that the anode press will experience a renaissance in the near future.

9:00 AM

COOLING OF GREEN ANODES AFTER FORMING: Werner K. Fischer[1]; Markus W. Meier[1]; *Mauriz Lustenberger*[1]; [1]R&D Carbon, Ltd., P.O. Box 362, Sierre CH-3960 Switzerland

The cooling process is limited by the temperature conductivity of the green anode. Experimental work and simulations indicate, that only a small outer crust is cooled down during the main cooling process, while the inner part of the anode body remains hot. This may result in frozen stresses, which can be reduced if the anodes are cooled with a higher temperature level of the cooling medium. No significant loss of cooling performance is observed. A lower forming temperature drastically reduces the heat flow from the inner part to the outside of the anode. The anodes can then be cooled by forced air convection in a wind tunnel during the transport to the anode storage. Therefore, anode cooling by water spraying or immersion in a water bath can be avoided. The requirement of lowering the forming temperature emphasizes the installation of an anode press.

9:25 AM

CONTROL OF PAH AND CTPV'S FOR ANODE MANUFACTURING PROCESS BY REGENERATIVE THERMAL OXIDATION: *Gerard Gosselin*[1]; Guy Drouin[1]; [1]Biothermica International, 3333 Boul. Cavendish, Suite 440, Montreal, Quebec H4B 2M5 Canada

Regenerative thermal oxidation process was applied to an anode paste plant. This plant has a non standard mixing configuration. Ko-kneader and intensive mixers operate in series. This configuration allows to increase petroleum coke and binder pitch temperatures prior to the first mixing stage with the Ko-kneader mixer. Then, the hot paste is sent to an intensive mixer that is operated as a mixer-cooler. By using water to cool down the paste, PAH (polycyclic aromatic hydrocarbons) and CTPV's (coal tar pitch volatiles) emissions increased to a level higher than usual, requiring a more efficient control. RTO (regenerative thermal oxidation) was selected as the more interesting scrubbing process. PAH and CTPV's emissions measurements after installation of the new equipment show a reduction of 99.9%.

9:50 AM BREAK

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EXHAUSTION AND SCRUBBING OF PITCH FUMES, AN ENVIRONMENTAL PROBLEM AT ALBRAS: *Paulo Douglas Vasconcelos*[1]; Andre Mesquita[2]; Joao Quaresma[2]; Daniel Cruz[2]; [1]Albras Aluminiol Brasileiro, ROD.PA483 KM21, Barcarena, PA 68447-000 Brasil; [2]Universidade Federal do Para, Centro Tecnologico, Av. Bernardo Sayao, s/n, Belem Brasil

Albras operates two anode plants with a capacity of approximately 280,000 mtpy using 40,500 mtpy of pencil pitch, which is used as a dry aggregate (coke) binder. In the green paste production, a fraction of pitch volatiles results in form of vapor (70ppm) that is released from the mixers, belt conveyor and anode vibrocompactor. These volatiles contain polyciclic aromatic hydrocarbons (PAH) that in certain concentrations are harmful to the health. Therefore the exhaustion and the treatment of these volatiles are strictly necessary to improve the workplace environment. The paper shows how the original inefficient wet scrubber was successfully substituted by a dry scrubber, designed in cooperation with the local Federal University. A mathematical model was developed to study the adsoption of fumes by ultrafine coke particles from the ball mill bag filter.

10:35 AM

CONVERSION OF A CLOSED FURNACE TO THE OPEN TYPE TECHNOLOGY AT ALUMINIUM BAHRAIN: *Jean-Claude Thomas*[1]; Jaffar G. Ameeri[2]; Philippe Breme[1]; Jean-Christophe Rotger[1]; [1]Aluminium Pechiney, Aluval, B.P.7, Voreppe F-38340 France; [2]Aluminium Bahrain, B.S.C. (C), P.O. Box 570, Manama Bahrain

As part of an expansion program of its smelter in Bahrain, Alba signed in 1995 a contract with Pechiney for the reconstruction of one of its closed furnaces in an open type one, inside the existing concrete casing. The furnace was stopped in May 1996 and restarted six months later after complete transformation. Further to production which has been increased by 34% at a low capital cost, this conversion has much improved the consistency and homogeneity of the baking parameters. The transformation required some modifications of the casing, in particular the construction of a central air cooled wall to separate the two bays. The new fluewall characterized by an unusual rectangular shape was optimized in detail thanks to an improved modelization of the internal gas flow.

11:00 AM

METHODS TO PREDICT FLUE LIFE AND FLUE FAILURE RATES IN ANODE BAKING FURNACES: *Gerald F. Chovanec*[1]; [1]Century Aluminum of West Virginia, Primary Products, P.O. Box 98, Ravenswood, WV 26164 USA

Methods to predict flue life/failure rates in anode baking furnaces have been developed. One method incorporates extrapolation of cumulative percent failure graphs using linear regression; the second method is based on a correlation between flue condition ("flue severity") and flue age. Failure patterns were analyzed for flue groups installed over a period of about eight years. Cumulative percent flue failure curves for groups ranging in size from 11 to 322 flues displayed "near normal" failure distributions. By "backtracking" failure data, it was deduced that flue life/failure rate would have been satisfactorily predictable after about 25 - 30% failure; below this level, predictions would have been erratic. To provide an alternative method of flue failure predictions for groups in which an insufficient number, or no failures have occurred, a relationship between "flue severity" and flue age was developed and provides a satisfactory first approximation of flue failure rates.

11:25 AM

FLUE GAS MANAGEMENT: *W. Leisenberg*[1]; [1]Innovatherm, GmbH + Company, Butzbach D-35510 Germany

Because of environmental demands In the last time flue gas analysis and control became more important. Contradicting goals as are: a minium of flue gas volume, sufficient heat transfer to the preheating zone, maximum fuel efficiency and perfect volatile combustion ask for better knowledge of the process and for advanced strategy of the flue gas control and the fuel injection, especially for furnaces with narrow flues. Furthermore the implications of CO and NOx content in the flue and the way of fuel injection as are short or long pulses and the addition of primary combustion air have to be taken in account and ask for a control strategy, which regards all those parameters and should be called a flue gas management rather than a control. In the last year investigations have been done on this objective and the results will be presented on the session.

CAST SHOP TECHNOLOGY: DC Casting/ Modeling I

Sponsored by: Light Metals Division, Aluminum Committee
Program Organizers: Y. Sahai, The Ohio State University, Dept. of Mats. Sci. and Eng., Columbus, OH 43210-1179 USA; James O'Donnell, Commonwealth Aluminum, Dept. of Eng., Louisville, KY 40202 USA

Tuesday AM Room: 6C
March 2, 1999 Location: Convention Center

Session Chair: Dr. Yogesh Sahai, Ohio State University, Columbus, OH 43210-1179 USA

8:30 AM

INTERPRETATION OF THE BLEED OUT PHENOMENON OF EXTRUSION INGOT CASTING APPLYING THE MATHEMATICAL

MODEL ALSIM: *Bjorn Rune Henriksen*[1]; Einar K. Jensen[1]; Dag Mortensen[2]; [1]Elkem ASA Research, P.O. Box 8040 Vaagsbygd, 4602 Kristiansand, Vest-Agder Norway; [2]Institute for Energy Technology, P.O. Box 40, 2007 Kjeller, Lillestrøm Norway

The DC-casting process has been continuously improved with respect to ingot quality and recovery since its invention. The main challenge at the Elkem Lista cast house was to reduce the scrap rate due to billet bleed out in the start-up phase. The aim of this investigation was to understand the mechanism of bleed out and to find actions to avoid this phenomenon. Based on experimental casting trials and corresponding mathematical modeling a mechanism for billet bleed out is proposed. The results from ALSIM and experimental observations (micographs, temperature measurements) show that one of the most important factors affecting the bleed out is the filling of the mold table. The effect of starting block geometry/material, casting speed/temperature, starting block position and hot top design is studied as well.

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DETERMINATION OF THE THERMAL BOUNDARY CONDITIONS DURING ALUMINUM DC CASTING FROM EXPERIMENTAL DATA USING INVERSE MODELING: I.J. Opstelten[1]; J.M. Rabenberg[1]; [1]Koninklijke Hoogovens N.V.; P.O. Box 10000, 1970 CA IJmuiden, The Netherlands

The work described in this contribution is part of the EMPACT project. In this project several European partners (both from industry and university) have joined to develop tools for improving the casting of aluminum ingots. It involves the use and development of mathematical models which describe the micro- and macro segregation, the fluid flow and the thermo-mechanical behavior of the ingots. An accurate description of the thermal boundary conditions is of paramount importance for the correct prediction of the casting processes. Moreover, these boundary conditions serve also as an important control parameter in practice. Until now the heat transfer data obtained from immersion quenching experiments or semi-empirical relations are frequently used in the numerical models. The conditions during actual casts can differ substantially though, from the conditions for which this heat transfer data was obtained. Recently inverse modeling techniques have been used to obtain the thermal boundary conditions from thermocouple measurements during an actual cast. Although this seems the best way to obtain thermal boundary conditions for actual casting conditions, it is rather impractical when the influence of a number of parameters is to be established. In the present study the influence of several practical parameters on the thermal boundary conditions are experimentally determined. To this end the temperature-time history is measured at several locations inside an aluminum test block during steady-state waterfilm quenching. These measurements are input to an inverse model, which finds the thermal boundary conditions. The influence of casting speed, aluminum alloy type, cooling waterflow rate and water temperature, surface structure and waterfilm generator type is thus investigated. Several results of these measurements and the inverse modeling process will be shown.

9:20 AM

MECHANISMS OF SURFACE FORMATION DURING DIRECT CHILL (DC) CASTING: *Steinar J. Benum*[1]; Arild Håkonsen[1]; [1]Hydro Aluminium A.S., R&D Materials Technology, P.O. Box 219, Sunndalsoera, Sunndal N-6600 Norway

The mechanisms of surface zone formation during DC casting were summarised by K. Buxmann in 1974 (Metall). After his overview, changes have been utilized both in casting technology as well as knowledge of the solidification process. The present paper is and review of the mechanisms explained by Buxmann put in light of new casting technology. The paper emphasises the major change in casting technology that occurred when the air/gas-slip technology was developed by Showa early in the 1980's. The most characteristic of this process is the large meniscus constructed by detgas pocket between the metal and the mould. There are two segregation phenomena connected to the meniscus; a) meniscus segregation and b) change in meniscus shape. The first phenomenon is a metallostatic driven segregation that occurs when the pressure in the metal becomes larger than the additive pressures from the surrounding atmosphere, i.e., air pressure and meniscus strength. This segregation mechanism is similar to that often associated with Bergmann zones (Bergmann, J. of Metals (1973)). The second segregation phenomenon is given by the fluctuations of the meniscus itself. The size of the meniscus makes it susceptible to pertubations caused by changes in metal level and gas pressure. The resulting movements affect both the segregation pattern as well as the surface topography.

9:45 AM

COUPLED STRESS, THERMAL AND FLUID FLOW MODELLING OF THE START-UP PHASE OF ALUMINIUM SHEET INGOT CASTING: *Hallvard G. Fjær*[1]; Dag Mortensen[1]; Arild Håkonsen[2]; Einar A. Sørheim[1]; [1]Institute for Energy Technology, Mats. and Corrosion Technology Dept., P.O. Box 40, Kjeller N-2007 Norway; [2]Hydro Aluminium, R&D Materials Technology, P.O. Box 219, Sunndalsøra N-6601 Norway

The start-up of the DC-casting process of aluminium sheet ingots is a complex process where the development of temperatures, melt flow and deformations and stresses in the solid are essentially coupled phenomena. This work focuses on the influence of thermally induced deformations on the heat transfer at the ingot surfaces, which in particular involves development of an air gap between the ingot and the starting block as well as water intrusion into this gap. It also involves development of air gaps at the mould surface. These mechanisms are discussed and investigated by transient 3D simulations involving coupled stress, thermal and fluid flow modelling. This coupling has been implemented by communication between submodels which may run on different CPUs in a heterogeneous computer network. The coupled model have been applied on the casting of commercial size sheet ingots. Calculated results are compared with temperature measurements.

10:10 AM

EFFECT OF AS-CAST MICROSTRUCTURE AND SUBSEQUENT PROCESSING ON BANDING IN ROLLED Al-SHEETS: *Trond Furu*[1]; Hans Erik Vatne[1]; [1]Hydro Aluminium A.S., R&D Mats. Tech., P.O. Box 219, Sunndalsøra, Sunndal N-6600 Norway

Typical casting defects of rolling ingots of AA1XXX series alloys have been investigated. The effect of alloy chemistry (focused on 1050 and 1200 type alloys), grain refinement practice and casting conditions have been investigated and discussed. The most common defects are fir-tree structures and feathery crystals, which both may lead to streaks after rolling and etching/anodising. The fir-tree structures are influenced by cooling rate, grain refinement procedure and Fe:Si ratio (and amount). Feathery crystals are also influenced by grain refinement practice and melt temperature. In addition, another type of rolling defect was investigated; edge cracks. This rolling defect is not directly linked to a casting defect, but certainly to the quality and microstructure of the rolling ingot.

CREEP BEHAVIOR OF ADVANCED MATERIALS FOR THE 21ST CENTURY: Microstructure and Mechanisms III

Sponsored by: ASM International: Materials Science Critical Technology Sector, Flow & Fracture Committee, Structural Materials Division, Mechanical Metallurgy Committee, Materials Processing and Manufacturing Division, Powder Metallurgy Committee

Program Organizers: Rajiv S. Mishra, University of California, Dept. of Chem. Eng. & Mats. Sci., Davis, CA 95616 USA; Amiya K. Mukherjee, University of California, Dept. of Chem. Eng. & Mats. Sci., Davis, CA 95616 USA; K. Linga Murty, North Carolina State University, P.O. Box 7909, Raleigh, NC 27695-7909 USA

Tuesday AM Room: 15A
March 2, 1999 Location: Convention Center

Session Chair: M. McLean, Imperial College of Science, London, England; G.S. Daehn, Ohio State University, Columbus, OH, USA

8:30 AM INTERMETALLICS

8:30 AM INVITED PAPER

MECHANISMS OF PRIMARY AND SECONDARY CREEP IN NEAR-GAMMA TiAl ALLOYS: *Thomas R. Bieler*[1]; Dong Yi Seo[1]; [1]Michigan State University, Mats. Sci. and Mech., 3536 Eng. Bldg., East Lansing, MI 48824-1226 USA

Primary and secondary creep has been measured in a number of near-gamma TiAl alloys and in a polysynthetically twinned (PST) crystal (representing a single unit of lamellar microstructure). The PST crystals exhibit activation energies from temperature change tests between 130 and 190 kJ/mol, which are about half of the activation energies commonly measured in polycrystal specimens. Normal transients after temperature or stress changes are observed in both PST and polycrystal specimens. In polycrystals, two stages of primary creep deformation are evident in measured data, an early and rapid process that is exhausted in the first 0.2-0.5% strain, and a different process that dominates the deformation up through the minimum creep rate. From interrupted creep tests, the early process causes lamellar refinement, (i.e. a reduction in lamellar spacing), which correlates closely with the PST crystal deformation, and the second process does not affect the lamellar spacing significantly, but it has deformation para meters similar to secondary creep. The effects of differing heat treatment and alloy composition on the primary creep deformation processes indicate that primary creep resistance can be improved in some alloys by as much as 3 times with heat treatments, whereas addition of refractory elements, interstitials, and elements that stimulate formation of fine precipitates can increase the creep resistance by an order of magnitude. Analysis of deformation parameters indicate that the mechanisms of creep deformation are not effectively described with theory developed for metals and alloys.

8:55 AM INVITED PAPER

MECHANISMS OF CREEP DEFORMATION IN TITANIUM ALLOYS: *Michael John Mills*[1]; [1]The Ohio State University, Dept. of Mats. Sci. and Eng., 477 Watts Hall, 2041 College Rd., Columbus, OH 43210 USA

Due to their attractive strength and low density, conventional alpha-beta titanium alloys such as Ti-6242 are utilized extensively in rotating components in gas turbine engines. Relatively new TiAl alloys with slightly sub-stoichiometric compositions, are comprised of a lamellar microstructure consisting of fine laths of the intermetallic gamma and alpha-2 phases. These "gamma" alloys are presently under development for application in higher temperature, reciprocating components. In these applications, creep deformation is often a limiting material property in these two important titanium alloy systems. In this presentation, the microstructural origins of creep deformation and the sources of creep strength will be discussed for both alpha-beta titanium alloys at ambient and intermediate temperatures, as well as for gamma-TiAl at higher temperatures. Our understanding of the modes of deformation and important dislocation/interface interactions as revealed by TEM investigation will be presented. Attempts t o model these deformation modes in light of this microstructural information will also be described. Funding for this work has been provided by the Air Force Office of Scientific Research and by the National Science Foundation.

9:20 AM

CREEP AND MICROSTRUCTURE OF NEAR Γ-TiAl INTERMETALLICS: *A. DlouhΩ*[1]; K. Kucharova[1]; T. Horkel[1]; [1]Institute of Physics of Materials, Academy of Sciences of the Czech Republic, Zizkova 22, Brno 616 62 Czech Republic

Creep and microstructure of pure γ-phase and two-phase γ / α_2 intermetallic TiAl alloys are investigated. The basic creep data obtained in tension and compression in the temperature range 923-1100K and for applied stresses between 50 and 400MPa are presented. It is shown that, while the pure g-phase Ti-52at%Al alloy is brittle in tensile creep at 1100K and for applied stresses above 150MPa, the two-phase γ / α_2 fully lamellar Ti-48Al-2Cr-2Nb-1B (in at%) alloy exhibits a remarkable ductility at considerably lower temperatures. A conventional light microscopy, SEM and TEM were used to quantify the microstructure of the alloys before and after creep. A systematic study of the grain size revealed that a grain growth occurs during creep of Ti-52at%Al alloy while a grain refinement due to recrystallization is observed after creep in Ti-48Al-2Cr-2Nb-1B alloy. The difference in the creep behaviour of the investigated alloys is attributed to the different intensity of dislo cation glide, twinning and recrystallization, the microstructural processes which operate in the range of external conditions studied.

9:40 AM

CREEP/FATIGUE DEFORMATION AND CRACK GROWTH IN A Γ-TITANIUM ALUMINIDE TURBINE BLADE MATERIAL: *Kamran Nikbin*[1]; [1]Imperial College, Mech. Eng. Dept., Exhibition Rd., London SW7 2BX UK

In order to improve the performance of gas turbines there is a trend towards the use of higher strength to weight and stiffness to weight ratio materials. In this investigation the intermetallic, γ-titanium aluminide (γ-TiAl), which is a candidate material for blade and disc applications, is examined. The intermetallic g-TiAl is a candidate material for high strength to weight applications in advanced gas turbines. However it exhibits limited creep ductility at temperatures up to about 650ϒC and there is a need to establish it's tolerance to the types of stress state generated at stress concentrations. Different batches of the material were tested. Most high temperature gas turbine components experience multiaxial stress states during operation at sites of stress concentration caused by thermal gradients, holes and sharp changes in section. In order to determine the useful lifetimes of these components at elevated temperatures data from uniaxial bar, notched bar and fracture mechanics specimens are analysed taking into account the effects of multiaxial states of stress which are present for the different geometries. Subsequently metallographic examination was carried out on failed specimens. Significant results have been achieved in the experimental and the modelling aspects of failure of materials under a tri-axial state of stress. From notch rupture tests, fatigue crack growth tests at 700ϒC and supporting microstructural evidence it has been found that the alloy has good notch strengthening properties. However it has also been shown that it has unpredictable crack initiation and growth properties. In addition the radical variation of properties from batch to batch which apparently have the same nominal composition and heat treatment suggests that further work is needed to determine the suitability of this alloy for turbine blade applications.

10:00 AM

A NEW SUGGESTION OF CREEP DEFORMATION MECHANISM OF TiAl: *Soo Woo Nam*[1]; Han Seo Cho[1]; [1]Korea Advanced Institute of Science and Technology, Dept. of Sci. and Eng., 373-1 Kusong-dong Yusong-gu, Taejon, ChungNam 305-701 Korea

It is well known that the steady-state creep deformation mechanism of pure metals and certain solid solution alloys is controlled by the

dislocation climb process with the help of self-diffusion. Therefore, the creep deformation activation energy in the steady-state is measured and known to be that of self-diffusion. However, in the primary stage, the dislocation density is increasing with primary strain and the activation energy in this stage is measure to be lower than that of steady-state. This is because of the fact that the higher effective stress (since the dislocation density is lower) in the primary stage is responsible in lowering the apparent activation energy, Qapp = Qo σeV, where Qapp is the apparent activation energy, Q_o is the self-diffusion activation energy, σ_e is the effective stress and V is the activation volume. In case of lamella TiAl, same as in metals the normal primary creep stage is observed. However, as the primary strain increases, it is found that the dislocation density is decreasing but the primary creep activation energy is increasing from the value of the activation energy of self-diffusion of Ti in TiAl (300kJ/mol) to the value of about 400kJ/mol which is measured to be the creep activation energy of TiAl obtained using the steady state creep rate. This decreasing dislocation density in primary creep stage is the opposite phenomenon to that of common metals and the higher activation energy than that of self-diffusion is also different from the cases of metals. Small amount of prestrain is found to be responsible for the reduction of the initial dislocation density and this prestrained specimen shows significantly reduced primary creep strain and the creep activation energy in the primary stage is also measured to be about 400kJ/mol. During creep deformation of lamella TiAl, as the initial dislocation density is decreasing, α_2 phase is found to be transforming to γ phase to generate new dislocations which contribute creep deformation. In other words, this phase transformation is the source of the dislocation generation for the continuous creep deformation. Therefore, the phase transformation is suggested to be one of the rate controlling processes whose activation energy is thought to be higher than that of self-diffusion, i.e., about 400kJ/mol.

10:20 AM INVITED PAPER

CREEP DEFORMATION IN DAMAGE TOLERANT NIOBIUM ALUMINIDE INTERMETALLICS: *R. W. Hayes*[1]; F. Ye[2]; W. O. Soboyejo[2]; [1]Metals Technology, Inc., 19801 Nordhoff St., Northridge, CA 91324 USA; [2]The Ohio State University, Dept. of Mats. Sci. and Eng., 2041 College Rd., Columbus, OH 43210 USA

The micromechanisms of creep deformation will be elucidated for a new class of damage tolerant niobium aluminide (Nb3Al-xTi-yMo-zCr) intermetallics with partially ordered two phase (B2 + orthorhombic) crystal structures. These alloys have been shown to have attractive combinations of room temperature ductility (5-30%), fracture toughness (40-100 MPa $m^{-1/2}$) and fatigue resistance. However, there have been no published reports of the elevated-temperature creep behavior of niobium aluminides. Primary and secondary creep rate data will be presented for the temperature range (between 650 and 750°C) in which uncoated alloys have been shown to have the potential for structural applications. Activation energies and creep exponents obtained from stabilized orthorhombic + B2 microstructures will also be compared with previously reported data for B2 and orthorhombic intermetallics. The implications of the results will be discussed for potential intermediate-temperature structural applications of niobium aluminide intermetallics.

10:45 AM BREAK

10:50 AM THRESHOLD STRESS

10:50 AM INVITED PAPER

INTERPRETATION OF THRESHOLD STRESSES AND OBSTACLE STRENGTHS IN CREEP OF PARTICILE STRENGTHENED MATERIALS: *Jeffery C. Gibeling*[1]; [1]University of California, Dept. of Chem. Eng. and Mats. Sci., One Shields Ave., Davis, CA 95616 USA

Virtually all descriptions of creep deformation in particle-strengthened materials rely on the introduction of some empirical quantity with units of stress. These are variously known as threshold stresses, obstacle glide resistances, detachment stresses and athermal stresses. The purpose of these terms is to appropriately scale the data so that parameters such as stress exponents and activation energies conform to expected values based on an assumed deformation mechanism. However, the theoretical justification and physical interpretation of these stress terms is often limited, and the experimental methods for deriving the values of these quantities is usually indirect. Advances in the application of new materials will require a more thorough fundamental understanding creep in these advanced materials coupled with appropriate models of deformation. The different interpretations of threshold stresses and obstacle strength parameters for dispersion-strengthened metals and metal matrix composites are reviewed. The experimental evidence in support of the various approaches to describing creep in particle strengthened materials and the methods for determining parameter values are examined. Particular attention is given to the assumption of constant structure creep behavior in identifying an appropriate stress exponent and the need to use a value of 8 with caution. The importance of considering mobile dislocation density and the interactions of multiple dislocations with particles is discussed. The limitations of using similar approaches for dispersion strengthened metals and metal matrix composites, which have very different particle size scales, are explored. Finally, the need to properly account for evidence of creep transients is emphasized.

11:15 AM INVITED PAPER

MICROSTRUCTURAL THRESHOLD EVENTS, BACK STRESSES AND MINIMUM CREEP RATES - A NEW WAY OF INTERPRETING CREEP IN ADVANCED ENGINEERING MATERIALS: *Gunther Eggeler*[1]; [1]Institut für Werkstoffe-Werkstoffwissenschaft, Ruhr-Universität, Bochum

Traditional approaches to rationalize creep of materials use minimum creep rate data in an attempt to study and understand their dependence on stress and temperature. Steady state creep, power law creep and the back stress approach are famous concepts which have been used to describe creep deformation mechanisms of materials over the last three decades. While these concepts have not lost any of their power in helping to analyze creep behavior there are cases where more is required to understand what actually controls creep. Thus microstructural threshold events on different size scales are important in creep of many advanced materials like (i) detachment of dislocations from oxide dispersoids in ODS alloys, (ii) breakage of fibres in short fiber reinforced MMCs, (iii) cutting of gamma prime particles in superalloy single crystals and (iv) the onset of dynamic recrystallization during creep in near gamma titanium aluminides. Creep is generally the result of the coupling of a number of interconnected microstructural processes and often microstructural threshold events play a key role. As deformation proceeds macroscopic (classical) back stresses build up and counteract the applied stress. But back stresses have a microstructural origin, they are not constant throughout the creep process and what microstructural and mechanical consequences this has is a first important point which will be discussed in the present paper. In the light of microstructural threshold events macroscopic back stresses which counteract the applied stress represent the driving forces which trigger the onset of threshold events. This is a second important point which will be highlighted in the paper. And finally, microstructural threshold events can result in microstructural changes which influence the creep process. In addition to a general analysis of how microstructural threshold events can be integrated into creep models two examples of advanced engineering alloys where microstructural threshold events are important are presented in more detail, (i) creep in short fiber reinforced aluminium alloys and (ii) creep of gamma prime strengthened super alloy single crystals. One important general conclusion is that progress in the understanding of creep mechanisms in advanced engineering alloys must be guided by state of the art microstructural analysis. Merely fitting data to classical concepts does not help to progress the field of creep of advanced engineering alloys. State of the art creep models for advanced engineering materials should reflect all important elementary microstructural processes including threshold events and not only rationalize the stress and temperature dependence of the minimum creep rate but also describe the shape of individual creep curves.

11:40 AM INVITED PAPER

THRESHOLD STRESSES IN HIGH TEMPERATURE YIELDING AND CREEP: A CRITICAL REVIEW: *M. Heilmaier*[1]; B. Reppich[2]; [1]University of Western Australia, Dept. of Mech. & Mats. Eng., Nedlands 6907 Australia; [2]University of Erlangen-Nürnberg, Institute of Mats. Sci., Erlangen D-91058 Germany

At low temperatures incoherent oxide particles introduce a yield strength increment for dislocation glide due to Orowan bypassing, called

threshold stress σ_{th}. However, at high temperatures such a true threshold does not exist. In contrast, the material deforms even under the lowest stress applied. Therefore, the Orowan process has lost its predominating microstructural significance. Instead, models for climb threshold developed in the past with respect to different particle shapes and climb geometries will be discussed by introducing a universal parameter called climb resistance R. An essential result for most oxide dispersion strengthened (ODS) alloys is that the detachment of the partially relaxed dislocation from the particle-matrix interface controls the creep kinetics. As a consequence, our concept tackles creep thresholds in two steps: first, we associate σ_{th} with the apparent particle hardening contribution σ_p to realize a creep rate in the particle-strengthened alloy equivalent to that of the corresponding single-phase matrix. Second, the course of σ_p with respect to strain rate is modelled by applying the above mentioned particle hardening mechanisms. We exemplify and verify our approach with selected ODS platinum-, nickel- and iron-based alloys. [1]Permanent address: Institute of Solid State and Materials Research Dresden, D-01069 Dresden, Germany

FLUID-FLOW PHENOMENA IN METALS PROCESSING: Continuous Casting

Sponsored by: Extraction & Processing Division, Process Fundamentals Committee, Jt. Extraction & Processing Division and Materials Processing and Manufacturing Division, Synthesis, Control, and Analysis in Materials Processing Committee, Light Metals Division

Program Organizers: Nagy El-Kaddah, University of Alabama, Dept. of Met. & Mats. Eng., Tuscaloosa, AL 35487-0202 USA; Stein Tore Johansen, SINTEF Materials Technology, Processing Metallurgy & Ceramics, Trondheim, NTH N-7034 Norway; David G. Robertson, University of Missouri-Rolla, Dept. of Metall. Eng., Rolla, MO 65409-1460 USA; Vaughan Voller, University of Minnesota, Saint Anthony Falls Lab., Minneapolis, MN 55414-2196 USA

Tuesday AM Room: 2
March 2, 1999 Location: Convention Center

Session Chairs: James W. Evans, University of California, Dept. of Mats. and Min. Eng., Berkeley, CA 94720 USA; Achilles Vassillcos, US Steel Technical Center, Monroeville, PA 15146 USA

8:30 AM

COMPUTATIONAL FLUID DYNAMICS MODELLING OF TUNDISHES AND CONTINUOUS CASTING MOULDS: *Ian Hamill*[1]; Tracy Lucas[2]; [1]CFX International, AEA Technology, 8.19 Harwell, Oxon OX11 ORA England; [2]Kvaerner Metals Continuous Casting, Prince of Wales Rd., Sheffield, Yorks S9 4EX England

Issues of importance in the area of continuous casting centre around product quality. This can be affected by particle inclusions transported into the mould from upstream processes and by draw-down of particles from the meniscus. Turbulence of the meniscus can increase the latter, and is also detrimental to product surface quality. Suitably validated Computational Fluid Dynamics (CFD) modelling can provide the operator with an efficient tool with which to investigate the effects of changes to the design and operation of the caster and associated plant. In this paper, examples will be presented of the use of the CFD software, CFX, to simulate: inclusion motion and removal in tundishes and continuous casting moulds using an algebraic slip model; free-surface shape and turbulence in the mould using deforming meshes; solidification in the mould using a fixed-grid, source-based method; argon gas injection through a submerged entry nozzle using a full multiphase model. The CFD simulations are complemented by detailed Particle Image Velocimetry measurements performed on a full-size water model of a thin-slab mould and upper strand. Close agreement is demonstrated between the predictions and experiments.

8:50 AM

SIMULATIONS OF GAS ENTRAINMENT IN A CONTINUOUS CASTING TUNDISH: *D. Morton*[1]; S. Louhenkilpi[1]; [1]Helsinki University of Technology, Dept. of Mats. Sci. and Rock Eng., P.O. Box 6200, Hut 02015 Finland

In continuous casting operations, metal is transferred from a ladle to the tundish via a submerged shrouding tube. When changing the ladle, blockage of the outlet is a common problem. In clearing such blockages, the nozzle must be removed from the ladle outlet so that an oxygen lance can be applied. Until the nozzle can be replaced, the outlet stream becomes a free jet that impacts the surface of the molten material contained in the tundish. Such impacts are undesirable since reoxidation of the metal increases the number of inclusions found in the cast product. This effect is significant enough that it often results in several tons of low-grade steel. In this paper, we shall present the results of numerical study of gas entrainment due to a continuous stream. CFD simulations have been performed using a "finite volume" approach that includes improved techniques for modell in extreme free surface deformation and the effect of surface tension. The numerical results clarify the mechanism by which a continuous stream carries an annular film of gas beneath the surface of the receiving fluid. Furthermore, the simulations predict the growth of instabilities on the surface of this film and subsequent break up to form air bubbles. Finally, the results of the study are used to make estimates of the bubble sizes entrained in the tundish when feed from a ladle occurs as a continuous open stream.

9:10 AM

ELECTROMAGNETIC METHODS TO REDUCE CLOGGING IN TUNDISH NOZZLES: Laszlo Kadar[2]; *J. D. Lavers*[1]; [1]University of Toronto, Dept. of Elect. & Computer Eng., Toronto, Ontario M5S 3E4 Canada; [2]Hatch Associates, 2800 Speakman Dr., Mississauga, Ontario L5K 2R7 Canada

This paper discusses the potential of electromagnetic forces to reduce, and for certain situations to eliminate, the stagnation regions that lead to clogging of tundish nozzles. In the continuous casting of aluminum killed steel the tundish nozzle often experiences clogging problems. Water model studies have shown that the clogging problem is dependent on the flow pattern in the nozzle entry region. In particular, the flow can separate at the entrance to the nozzle which leads to the development of a recirculation region. Although a nozzle can be designed such that no recirculation develops, even a small misalignment from the vertical positioning of the nozzle may render the design ineffective. To reduce the possibility of nozzle clogging, the recirculation zone must be reduced or eliminated. This may be achieved by moving the fluid downwards or raising the turbulence level in the separation region. In aerodynamics, this is achieved by blowing or introducing suction in the stagnation zone. In the case of a tundish nozzle, a similar effect can be achieved by using electromagnetic forces. To generate the required electromagnetic force, two systems are considered. The first is based on injecting a DC current; the second by using electromagnetic induction. Both methods are described in this paper. Order of magnitude calculations are provided to illustrate that both methods are essentially feasible. The performance of each method in terms of modifying the turbulent flow characteristics in the nozzle entry region is then examined using a numerical model. It is shown that both methods can greatly reduce the recirculation zone. A cylindrical nozzle was chosen for the model studies since it represents a worst case situation. However, the widely used radius entry nozzle was also considered. On the basis of the model studies, it was concluded that whereas both of the proposed methods have the potential to reduce the troublesome recirculation zone, the induction method appears to be simpler in terms of practical implementation.

9:30 AM

RECENT RESULTS OF MODELING OF METAL DELIVERY SYSTEMS USED IN EM AND DC CASTING OF ALUMINUM: W. Kinzy Jones[1]; Dong Xu[1]; *J. W. Evans*[1]; [1]University of California, Dept. of Mats. Sci. & Mineral Eng., 585 Evans Hall #1760, Berkeley, CA 94720 USA

It is well understood that the flow of liquid metal in the mold region of the ingot can have a notable effect on the overall solidification behavior. Previously our group has characterized the flow in this region in a water model using particle imaging velocimetry. The flow is significantly effected by the specifics of the metal delivery system, i.e. size, geometry, used during the cast. Recently, a time-averaged 3-D numerical model of the nozzle, combo bag and sump region has been developed and its validity has been tested against the experimental data. A deformable free surface was built into the numerical model to better represent the actual surface of the physical sump. Cases were compared for different sized combo bags as well as bags that have blocked. The results show good agreement between the physical and mathematical models.

9:50 AM

MATHEMATICAL AND PHYSICAL MODELLING OF STEEL FLOW IN TWIN ROLL/HORIZONTAL BELT CASTERS: *R. I. L. Guthrie*[1]; R. P. Taveres[1]; P. Q. Netto[1]; [1]McGill University, McGill Metals Processing Center, M.H.Wong Eng. Bldg., Montreal H3A 2B2 Canada

Near net shape casting technology is one of the most important areas for research and development in the iron and steel industry today. Two of the key elements in the successful design and operation of thin strip casting machines are metal delivery systems and productivity. Productivity, in turn, is related to the rate and net amount of heat that can be extracted by a particular machine. This work demonstrates the complex interactions that take place between metal flow and solidification, depending on the nozzle delivery system, the rate of heat extraction, and the physical configuration of the caster.

10:10 AM BREAK

10:30 AM

DESIGNING OF SUBMERGED ENTRY NOZZLE FOR SLAB CONTINUOUS CASTER WITH FLOW AND SOLIDIFICATION ANALYSIS: *Masafumi Morishita*[1]; Hirofumi Tai[1]; Toshiya Miyake[1]; [1]Kobe Steel, Ltd., 2222-1 Ikeda, Onoe-cho, Kakogawa, Hyogo 675 Japan

The shape of the Submerged Entry Nozzle for Kakogawa No. 4-2 slab continuous caster was optimized in order to prevent corner cracking while high through-put casting. Numerical simulations about the flow and solidification in the mold was successfully applied for the optimization.

10:50 AM

TWO PHASE FLOW NUMERICAL SIMULATION OF MOLTEN STEEL AND ARGON GAS IN CONTINUOUS CASTER MOLD: *Noriko Kubo*[1]; Jun Kubota[1]; [1]NKK Corporation, Materials & Processing Research Center, Steelmaking Laboratory, Kokan-cho Fukuyama, Hiroshima 721-8510 Japan

For steel continuous castings, it is important to control molten steel velocity at meniscus, since it is closely related to surface defects of the resultant products. Argon gas is injected into the mold with the molten steel to prevent clogging of the submerged entry nozzle. To investigate the influence of argon gas on molten steel flow in the mold, numerical simulations have been carried out by using a two phase CFD model. Simulation results indicate a strong impact of argo gas on the molten steel flow. As argon gas bubbles ascend near the nozzle by buoyancy, they entrench molten steel upward to the meniscus. As a result, the molten steel flows outward to the narrow face of the mold at meniscus. This flow direction is opposite to the case without argon gas, in which the molten steel flows inward from the narrow face of the mold at meniscus.

11:10 AM

NUMERICAL SIMULATION OF FLUID MOTION IN CONTINUOUS CASTING PROCESS WITH LINEAR MOTORS: *Ch. Strohm*[1]; Y. Couvat Du Terrail[1]; S. A. Rotelec[1]; M. C. Nove[1]; [1]EPM MADYLAM, ENSHMG, BP 95, 38402 Saint Martin d'Herdes, Cedex France

A specialized software has been developed for the numerical simulation of the liquid metal flow control in the particular case of the continuous casting processes. The device includes linear motors placed at the upper level of the ingot in order to control the metal speed and direction. Electromagnetic forces are calculated in three dimensions with a finite element program based on A, A-V formulation. Hydrodynamic in the ingot is solved in two dimensions using a finite different scheme using w-Y formulation. The weak coupling between electromagnetic and hydrodynamic is realized by interpolating the Laplacian forces on the nodes of the hydrodynamic grid: firstly as a mean efficient value on each node and secondly as a time dependant vector pulsating at low frequency. Then, a strong coupling is implemented by adding to the weak coupling two alternate models. In the first one, the induced currents are computed again in the hydrodynamic scheme, assuming no changes in the magnetic field. In the second approach all the electromagnetic variables are calculated again in the finite element program. The electromagnetic results have been compared to experimental trials with an empty ingot. Numerical comparisons with 3D fluent calculations have been done for the fluid flow validation.

11:30 AM

MODELING OF ELECTROMAGNETIC STIRRING IN CONTINUOUS CASTING OF STEEL: *Thinium T. Natarajan*[1]; Nagy El-Kaddah[2]; [1]U.S. Steel, Technical Center, 4000 Technical Center Dr., Monroeville, PA 15146 USA; [2]The University of Alabama, Dept. of Metall. Eng., Box 870202, Tuscaloosa, AL 35487-0202 USA

Electromagnetic stirring is widely used in continuous casting of steel as a means to improve homogeneity of cast billets and strands. The degree of mixing in the molten pool strongly depends on the stirrer design and dimensions. This paper describes a new general formulation for modeling electromagnetically driven flow in three-dimensional induction systems, and its application to modeling electromagnetic and flow phenomena in sub-mold rotary stirring of square billets. This model is based upon finite element solution of current and magnetic scalar potential equations for computing the electromagnetic field and Navier-Stokes equations together with the k-e turbulent model for velocity and turbulent parameter calculations. The computed force field in the billet revealed that the billet corners are the source of vorticity of the force field, which drives the flow in the bulk. Effective mixing was found to be confined to the region surrounded by the stirrer, and the mixing intensity diminishes rapidly beyond the edges of the stirrer. The significance of these findings on the effectiveness of rotary stirring on melt homogenization and inclusion removal will be discussed.

GENERAL ABSTRACTS: Session 4 - Fatigue, Corrosion Fatigue and Wear

Sponsored by: TMS

Program Organizers: Garry W. Warren, University of Alabama, Dept. of Metals and Mats. Eng., Tuscaloosa, AL 35487-0202 USA; Ray D. Peterson, IMCO Recycling Inc., Irving, TX 75039 USA; Robert D. Shull, NIST, Bldg. 223 Rm. B152, Gaithersburg, MD 20899 USA

Tuesday AM — Room: 12
March 2, 1999 — Location: Convention Center

Session Chairs: Indranath Dutta, 93943 Naval Postgraduate School, Monterey, CA 93943 USA; Eric M. Taleff, The University of Texas, ASE/EM CO600, Austin, TX 78712-1063 USA

8:30 AM

THE EFFECTS OF RESIDUAL STRESSES ON FATIGUE CRACK INITIATION: Jonathan D. Almer[2]; *Jerome B. Cohen*[1]; Brian Moran[3]; [1]Northwestern University, Robert R. McCormick School of Engineering and Applied Science, 2225 North Campus Dr., MLSB/Room 2036, Evanston, IL 60208-3108 USA; [2]Linkoping University, Konstruktions Material, IKP (Mech. Eng. Dept.), Linkoping S-581 83 Sweden; [3]Northwestern University, Dept. of Civil Eng., Technological Institute, Room A332, 2145 Sheridan Rd., Evanston, IL 60208-3109 USA

X-ray diffraction and Finite Element (FE) analysis have been used to study crack initiation in the presence of residual stresses. Residual stresses were introduced into polished double-edge notched (DEN) 1080 steel specimens by prestraining and press-fit operations, and initiation was monitored during high-cycle fatigue tests using surface replicas. The local stress-strain behavior in the vicinity of the initiation sites was tracked using FE analysis. Microbeam x-ray diffraction measurements were also made in each phase of the steel to determine both residual macrostresses, which were compared with the FE computations, and microstresses. Microstresses were observed to fade rapidly during fatigue, while macrostresses relaxed less rapidly and were observed to strongly affect crack initiation behavior. This fatigue behavior was then correlated with the observed stresses using a traditional stress-life relationship which includes mean stress effects. This research was funded in part by the Office of Naval Research, Grant No. N00014-90-J-1374.

8:50 AM

FATIGUE OF A FORMULA I TITANIUM CONNECTING ROD: *Gregor K. Mori*[1]; Karl L. Maurer[1]; [1]Dept. of Failure Analysis, Franz-Josef-Str., Leoben 18 A-8700 Austria

During training for the Italian Formula I Grand Prix in Monza 1997 one of the racing cars had an engine defect. Investigations of the broken parts showed a fatigue failure of one of the titanium connecting rods. The crack was situated after one third of the shaft length near to the small eye at the piston. The fracture plane progressed perpendicular to the shaft axis indicating some bending or tensile stresses. However the fracture origin was at the inner edge of one of the flanges of the H-formed shaft of the connecting rod. Additionally there the fracture plane was under 45 ° to the shaft axis which indicated the presence of torsion stresses. A small crack of 150 µm length and app. 200 µm depth had to be opened to prove a torsion fatigue fracture. A failure analysis is given and the reasons for the appearance of torsion cracks in a connecting rod are presented.

9:10 AM

CORROSION-FATIGUE CRACK INITIATION MECHANISMS IN ALUMINUM ALLOYS: *P. S. Pao*[1]; S. J. Gill[1]; C. R. Feng[1]; [1]Naval Research Laboratory, Code 6312, 4555 Overlook Ave., SW, Washington, D.C. 20375 USA

The mechanisms of corrosion-fatigue crack initiation by pitting in high-strength 7000-series aluminum alloys were studied. The alloys used in this investigation were 7075-T7351 and 7050-T7451. Corrosion pits were formed in 3.5% NaCl solution by the electrochemical reaction between the constituent particles and the surrounding matrix. Depending on whether these particles were cathodic or anodic relative to the alloy matrix, the pits formed as a consequence of matrix (around cathodic particles) or particle (for anodic particles) dissolution. Because these particles tend to cluster parallel to the rolling plane in the rolling direction, significant pit growth from pit coalescence was observed following prolonged exposure in a salt water environment. The effect of pre-existing corrosion pits on fatigue crack initiation was investigated using blunt-notched fracture mechanics specimens (oriented in the short-transverse direction) to simulate rivet holes. Results to date indicate that the presence of corrosion pits can significantly shorten the fatigue crack initiation life and decrease the threshold stress intensity of the alloy by as much as 50 percent. Post initiation fractographic analyses further confirmed that, when corrosion pits were present, fatigue cracks always initiated from these pits. In the absence of pits, fatigue cracks initiated from large inclusions. The identification of the constituent particles, the mechanism of pit formation and growth, and the analyses of fatigue crack initiation kinetics are discussed.

9:30 AM

CORROSIVE WEAR BEHAVIOR OF 7075 ALUMINUM ALLOY USING SCRATCH TECHNIQUE: *Gustavo Vasquez*[1]; Shailendra K. Varma[1]; [1]The University of Texas at El Paso, Dept. of Metall. and Mats. Eng., El Paso, TX 79968-05620 USA

The corrosive wear behavior of 7075 aluminum alloy has been investigated using scratch test. Samples immersed in an electrolyte have been subjected to impact by a stylus containing a diamond Vickers indenter at its tip. The transient current developed due to the creation of a new bare surface exposed to the corrosive environment has been determined as a function of solutionizing time. The details of scratches produced by impact and continuous loading have been compared. SEM observations have been correlated to the transient current generated and grain size developed as a result of varying solutionizing time during the corrosive wear process. Results on 7075 aluminum alloys will be compared with those previously reported for 6061 and 2014 aluminum alloys under identical set of experimental conditions.

9:50 AM BREAK

10:00 AM

THE SLIDING WEAR MECHANISMS OF PTFE COMPOSITES: *Jaydeep P. Khedkar*[1]; [1]Louisiana State University, Dept. of Mats. Sci. and Eng. Program, Dept. of Mech. Eng., 2508, CEBA, Baton Rouge, LA 70803 USA

The tribological performance of polytetrafluroethylene (PTFE) and PTFE composites under fixed operating conditions has been examined. The role of individual filler material influencing the friction and the wear properties of PTFE is critically evaluated. The wear tests are carried out on a laboratory pin on disc type apparatus and these results are compared with those conducted on a mechanical seal test rig simulating industrial conditions. A detailed microstructural examination is carried out using SEM so as to detect the possible modes of failures. DTA analysis of the materials is also presented to study the relative heat absorbing capacity and thermal stability of the various composites. An attempt is made at correlating the DTA results with the tribological performance of the composites. Finally, the main objective here is to propose the dominant interactive wear mechanisms during sliding of PTFE and its composites.

10:20 AM

HOT ISOSTATIC PRESSING OF TUNGSTEN CARBIDE TO STAINLESS STEEL FOR USE IN HIGH ABRASION/CORROSION RESISTANT APPLICATIONS: *Adele Crystal Boone*[1]; [1]MIT Student, Dept. of Mats. Sci. and Eng., 77 Massachusetts Ave., Cambridge, MA 02139 USA

To successfully Hot Isostatic Press (HIP) tungsten carbide (94-WC, 6%Co) to 17-4 precipitation hardened stainless steel for the application of high abrasion/corrosion resistant separator blades through the use of interlayers. Investigated interlayers include nickel-, silver-, molybdenum-, and copper-based foils. Metal-ceramet matrices and the tiling of carbides were also explored. Hip is of great interest because it produces a superior bond to the current technique of vacuum furnace nickel-based brazing. HIPping enhances fatigue strength and tensile ductility, reduces the scatter in creep life, and reduces the foundry scrap and inspection costs.

10:40 AM

THERMAL SPRAY AND MECHANICAL PROPERTIES OF NANOSTRUCTURED OXIDE COATINGS: *Leon L. Shaw*[1]; Ruiming Ren[1]; Daniel Goberman[1]; Maurice Gell[1]; [1]University of Connecticut, Dept.of Metall. and Mats. Eng., 97 N. Eagleville Rd., U-136, Institute of Mats. Sci., Storrs, CT 06269 USA

Nanostructured coatings can provide significant improvements in wear and erosion resistance deriving from enhanced hardness and toughness. In this paper, Al2O3 - 13 wt.% TiO2 coatings formed via thermal spray approach using reconstituted nanosized Al2O3 and TiO2 powder feeds are described. The microstructure, microhardness, indentation toughness, grain size and wear resistance of the coatings from the reconstituted nano-powder feeds have been characterized and compared to those obtained from commercial coating counterparts. The properties of the coatings obtained from reconstituted nano-powder feeds are discussed and related to thermalspray conditions.

11:00 AM

STRUCTURE AND PROPERTIES OF PVD-COATINGS BY MEANS OF IMPACT TESTER: *E. Lugscheider*[1]; O. Knotek[1]; Christian Wolff[1]; Stephen Barwulf[1]; [1]University of Technology, RWTH-Aachen, Augustinebach 4-22, Aachen 52062 Germany

Machine parts like rolling bearings or gears are stressed during operation in a changing mechanical strain. This causes wear by impacts and wear by rolling which is marked by the so called surface ruin. The

appearance of surface fatigue is based upon structural transformation, cracking and cracking-growth processes and ends with the separation of debris particles caused by the above mentioned permanent changing strain. The final stage, which is equivalent to the component failure, is the so called pitting on the technical surface, which is characteristically named surface fatigue. The impact tester is used for detailed research about failure mechanisms of thin films. Statements about the adherence of hard material coatings under dynamic compressive stress can be made using this test method, due to the possibility to simulate some effects of rolling strain. Therefore a hard metal ball strikes with a frequency of up to 50 Hz onto the surface. The altitude stress can be varied to get a detailed evaluation of fatigue strength under reversal strain. Selected hard material coatings were analyzed after testing with the described method applying an impact force of 300 N, 500 N and 700 N. In the framework of this presentation MSIP (Magnetron-Sputter-Ion-Plating) coatings on titanium- and chromium basis were used. The fatigue defects and the results of this study will be discussed depending on structure and morphology of thin films.

11:20 AM

DIFFUSION-BASED MICROALLOYING OF ALUMINUM VIA REACTION SINTERING: *Paul D. Bishop*[1]; M.C. Chaturvedi[2]; Georges J. Kipouros[1]; William F. Caley[1]; [1]DalTech-Dalhousie University, Mining and Metlalurgical Engineering; 1360 Barrington St., Halifax, Nova Scotia B3J 2X4 Canada; [2]University of Manitoba, Mechanical and Industrial Engineering, 15 Gillson St., Winnipeg, Manitoba R3T 5V6 Canada

In an effort to improve the properties of aluminum-based alloys, microalloying with selected elements has proven to be a viable method. Despite the broad range of alloys and microalloying additions possible considered, most rely on traditional ingot metallurgy practices. In this study an alternative technique using powder metallurgy principles and a diffusion/reaction sintering procedure is described. The basis of the method is the pressing of an outer shell of material containing the source microalloying element, in mineral form, about an aluminum pre-pressed core. Subsequent super-solidus liquid phase sintering liberated the cationic species of interest and promoted diffusion into the core material. Samples of a ternary Al-Cu-Mg alloy, as well as Al-2014 were successfully microalloyed with Sn and Ag. The resulting materials were age hardened and examined for hardness and tensile properties. As well, the microstructures were evaluated using scanning electron microscopy and X-ray diffraction, and selected samples were subjected to wear testing. Results were comparable to those obtained using ingot metallurgy techniques, yet the method offered the processing flexibility associated with powder metallurgy processes. Thus, the technique is an attractive alternative when a controlled level, composition and location of microalloying is of importance.

GENERAL ABSTRACTS: Session 5 - Physical Metallurgy: Thermodynamics, Interfaces & Diffusion

Sponsored by: TMS

Program Organizers: Garry W. Warren, University of Alabama, Dept. of Metals and Mats. Eng., Tuscaloosa, AL 35487-0202 USA; Ray D. Peterson, IMCO Recycling Inc., Irving, TX 75039 USA; Robert D. Shull, NIST, Bldg. 223 Rm. B152, Gaithersburg, MD 20899 USA

Tuesday AM Room: 13
March 2, 1999 Location: Convention Center

Session Chairs: Saskia Duyvesteyn, University of Utah, Dept. of Metall. Eng., Salt Lake City, UT 84112 USA; Dennis D. Keiser, Argonne National Laboratory, Nuclear Technology, Idaho Falls, ID 83403-2528 USA

8:30 AM

CHEMICAL AND STRUCTURAL ENERGY OF B1 TYPE COMPOUND/AUSTENITE INTERFACE: *Zhi-Gang Yang*[1]; Masato Enomoto[1]; [1]Ibaraki University, Dept. of Mats. Sci., Nakanarusawa 4-12-1, Hitachi, Ibaraki 316-8511 Japan

Various inclusions in steel are B1 type compounds, cube-on-cube orientated with austenite. The interfacial energy between B1 compound and austenite may play an important role in controlling the nucleation of ferrite on inclusions. The semi-coherent interfacial energy is known as having both chemical component and structural component. The chemical energy is calculated by nearest neighbor broken bond method following Lee and Aaronson, and the structural energy is computed based on the misfit dislocation model following Spanos. The result indicates that both chemical component and structural component contribute significantly to the total interfacial energy, although the latter is larger. Especially, the anisotropy of chemical energy is much stronger than that of structural energy, consequently it dominates the wulff construction and corresponding equilibrium shape of B1 compound in austenite. The temperature dependence of the interfacial energy and the concentration profile across the interface are also studied in this work.

8:50 AM

VIBRATIONAL ENTROPY DIFFERENCES BETWEEN AUSTENITIC AND MARTENSITIC NiTi BY LOW TEMPERATURE INELASTIC NEUTRON SCATTERING: *P. D. Bogdanoff*[1]; B. Fultz[1]; S. Rosenkranz[2]; [1]California Institute of Technology, Engineering and Applied Sciences, 138-78, Pasadena, CA 91125 USA; [2]Argonne National Laboratory, Mats. Sci. Div., Argonne, IL 60439 USA

We report our measurements for the difference in vibrational entropy between the low temperature martensite and high temperature austenite phases of NiTi, as measured by low temperature inelastic neutron scattering. The low temperature phase exhibits significant anharmonicity in the temperature range 0 to 200K, as measured by the phonon density of states (DOS). The austenite DOS shows little change between room temperature and 580 K, which is consistent with previous work. Earlier work done at Caltech measured the vibrational entropy difference between austenitic and martensitic NiTi at 0.4±0.1 kB/atom using low temperature calorimetry, a result in agreement with literature values. Work supported by U.S. DOE DE-FG03-96ER45572 and US DOE, BES-MS, contract W-31-109-ENG-38

9:10 AM

ENTHALPY OF FORMATION IN BINARY LAVES PHASES: *Jiahong Zhu*[1]; C. T. Liu[1]; L. M. Pike[1]; P. K. Liaw[2]; [1]Oak Ridge National Lab., Metals and Ceramics Division, P.O. Box 2008 , MS 6115, Oak Ridge, TN 37831-6115 USA; [2]University of Tennessee, Dept. of Mats. Sci. and Eng., Dougherty Eng. Bldg., Knoxville, TN 37996 USA

Enthalpies of formation of Laves phases have been critically surveyed and reviewed. It was found that the bond characteristics in Laves phases are not necessarily metallic in nature for both non-transition metal Laves phases and Laves phases containing transition metals. There are metallic, covalent and ionic bonds, or a mixed metallic-covalent-ionic bond. A thermodynamic interpretation is offered to explain the size ratio limits for Laves phase formation. As the deviation from the ideal size ratio increases, the maximum negative enthalpy of formation decreases linearly, which is assumed to be due to the elastic strain energy expended in compressing the atoms. At RA/RB =1.03 and 1.65, the enthalpy of formation reaches zero. Further deviation in the RA/RB ratio will lead to the enthalpy of formation positive. Thus, the free energy of formation becomes positive, due to the negligible entropy of formation term. Therefore, Laves phases can only be stabilized in certain atomic size, RA/RB, ratios. The enthalpies of formation calculated by the semiempirical Miedema model is in good agreement with the available experimental data for transition-metal and Al lanthanide Laves phases. This means that Miedema's theory can be used to predict quantitatively, at least qualitatively, the enthalpies of formation of transition-metal and Al lanthanide Laves phase systems.

9:30 AM

INFLUENCE OF COHERENCY STRAIN ON INTERFACE MIGRATION: *Jong K. Lee*[1]; [1]Michigan Technological University, Dept. of Metall. Eng., 1400 Townsend Dr., Houghton, MI 49931 USA

For a long time, coherency strain is known to play a crucial role in interface migration and thus microstructural evolution during alloy processing, but its understanding has been frustrated with the mathematical complexity associated with elasticity. This work presents some fascinating results of the Discrete Atom Method, which is predicated upon the combination of statistical mechanics and linear elasticity. It is found that coherency strain induces interfacial waves whose dynamic activities drive a coherent interface to migrate. The wavelength of these waves is proportional to the ratio of the interfacial energy to the strain energy, but strongly depends on elastic constants, interface geometry, and diffusion temperature. The waves also act as a source for the introduction of fresh ledges necessary in a ledge growth mechanism, and also responsible for the formation of pits, huts, and domes encountered in epitaxially-grown thin films. In an anisotropic system, stress concentrations are built at the regions o f elastically hard directions. In such a case, the interface is found initially to move toward the elastically-hard phase. If it is in a highly non-equilibrium state, coherency-induced wave interactions can create deep grooves on the interface, eventually splitting precipitates into smaller particles. Role of coherency strain in ordering and segregation phenomena will be also discussed.

9:50 AM BREAK

10:00 AM
TIME-DEPENDENT DIFFUSION PATHS ASSOCIATED WITH TRANSIENT PHASES IN TERNARY SYSTEMS: *Carelyn E. Campbell*[1]; William J. Boettinger[1]; [1]National Institute of Standards and Technology, Metallurgy, Bldg. 223 A153, Gaithersburg, MD 20899 USA

Unlike the time-independent composition paths associated with infinite diffusion couples, the composition paths of semi-infinite and finite diffusion couples can be time-dependent. This time dependence can result in the formation and/or dissolution of transient phases in multicomponent systems. The ability to predict the presence of transient phases during the diffusion process is important for many industrial processes, including transient liquid phase bonding. Numerical simulations of semi-infinite diffusion couples are compared to simulations of infinite diffusion couples for ternary systems with three species having equivalent diffusivities and ternary systems having one fast diffusing specie. For the Ni-Al-B system, diffusion paths through single-phase (γ-FCC), two-phase (liquid + γ-FCC) and three-phase (liquid + γ-FCC + intermetallic $Ni_{20}Al_3B_{(6\text{-}12)}$) regions are analyzed.

10:20 AM
AN INTERDIFFUSION MICROSTRUCTURE MAP FOR GAMMA/GAMMA+BETA DIFFUSION COUPLES IN THE Al-Cr-Ni SYSTEM: *Huimin Amy Chen*[1]; *John Eric Morral*[1]; [1]University of Connecticut, Dept. of Metall. and Mats. Eng., 97 North Eagleville Rd., U-136, Storrs, CT 06269 USA

ABSTRACT NOT AVAILABLE

10:40 AM
HIGHER ORDER BOUNDARIES IN MULTIPHASE DIFFUSION COUPLES: *John Eric Morral*[1]; Huimin Amy Chen[1]; [1]University of Connecticut, Dept. of Metall. and Mats. Eng., 97 North Eagleville Rd., U-136, Storrs, CT 06269 USA

ABSTRACT NOT AVAILABLE

11:00 AM
RAPID PREDICTION OF TIME-TEMPERATURE-TRANSFORMATION DIAGRAMS OF LOW AND MEDIUM CARBON MULTICOMPONENT ALLOY STEELS BY A COMPUTER EXPERT SYSTEM: *Zhenbo Zhao*[1]; *Derek O. Northwood*[2]; Cheng Liu[3]; Yunxu Liu[3]; Qihui Zhu[3]; [1]University of Windsor, Mech. & Mats. Eng., 401 Sunset Ave., Windsor, Ontario N9B 3P4 Canada; [2]Ryerson Polytechnic University, Eng. & Applied Sci., 350 Victoria St., Toronto, Ontario M5B 2K3 Canada; [3]Jilin Institute of Technology, Mats. Eng., 76 Yanan Dalu, Changchun, Jilin 130012 PR China

A computer expert system for the rapid prediction of time-temperature-transformation (TTT) diagrams of low and medium carbon multicomponent alloy steels was established. The principle and methodology for the rapid prediction of TTT diagrams were described. Some critical points of transformation used to model the time-temperature-transformation diagrams of muticomponent alloy steels were represented as functions of alloy chemistry. The bay between the two C-curves (pearlite and bainite), as a function of alloy chemistry, can be predicted accurately in terms of the precise calculation of Bs temperature (a new equation of Bs temperature has been proposed). It is believed that the reasonable prediction can be achieved in much larger concentration ranges. The limitations of alloy chemistry in most of other models can be avoided effectively because a relatively larger range of alloy chemistry (Ni, Mn, W, Mo, Cr, Si, V, Co, Cu) were considered in most equations. The commercial application potential in the design of new multicomponent alloy steels was discussed also.

11:20 AM
THE EFFECT OF CU ON PHASE TRANSFORMATIONS IN LOW CARBON STEELS: Shaun Dilney[1]; Matthias Militzer[1]; [1]The Centre for Metallurgical Process Engineering, University of British Columbia, Vancouver, BC, V6T 1Z4 Canada

Increases in the level of residual Cu in steel scrap is forcing electric arc furnace steelmakers to process steel containing higher levels of Cu. Although Cu can be detrimental during processing, causing hot shortness, it can also be a beneficial alloying element, improving mechanical properties through precipitation hardening and grain size refinement. The aim of this work is to investigate the effect of Cu on the phase transformation kinetics of low carbon steels, containing 0.05wt% to 0.8wt%Cu. The austenite decomposition kinetics has been investigated with continuous cooling tests using a dilatometer and a Gleeble 1500 thermo-mechanical simulator. The study emphasizes the cooling conditions of a hot strip mill run-out table. Based on the experimental results, a model is proposed which accounts for the effects of composition, cooling rate, and austenite grain size on the austenite-to-ferrite transformation kinetics, the resulting ferrite grain size and the mechanical properties.

HIGH-TEMPERATURE SUPERCONDUCTORS: SYNTHESIS, FABRICATION AND APPLICATION: Applications & Tape Fabrication

Sponsored by: 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 USA; Pradeep Haldar, Intermagnetics General Corporation, 450 Old Niskayuna Rd., Latham, NY 12110 USA; Chandra Pande, Naval Research Lab, Mats. Sci. & Tech. Div., Washington, D.C. 20375-5000 USA

Tuesday AM Room: 18
March 2, 1999 Location: Convention Center

Session Chairs: Judith MacManus-Driscoll, Imperial College of Science & Technology, Centre for High Temperature Superconductivity, London, England SW7 2BZ UK; H. W. Neumuller, Siemens AG, Corporate R & D, Erlangen Germany

8:30 AM INVITED PAPER
HIGH TEMPERATURE SUPERCONDUCTIVITY: PROSPECT FOR ELECTRONIC APPLICATIONS: *Donald U. Gubser*[1]; [1]Naval Research Laboratory, Mats. Sci. & Tech., Code 6300, 4555 Overlook Ave., SW, Washington, D.C. 20375-5343 USA

High temperature superconducting (HTS) films are of sufficient quality and size to permit system demonstrations of superconductivity for a variety of electronic applications. The most prominent device structures are the high Q filters. These filters are used in base stations for

cellular communications where range and signal quality are important; in radar systems where high levels of discrimination are important; and in communication systems where weak signals are received. Another electronic application area for HTS materials is in Superconducting Quantum Interference Devices (SQUID) that are used for detection of weak magnetic anomalies and in low noise signal amplifiers. A description of superconducting materials and system requirements will be given for these applications. Important to the introduction of these materials is the development of low cost refrigeration systems. Status and specifications of refrigeration systems for these applications will also be presented.

8:50 AM INVITED PAPER

DESIGN OF SUPERCONDUCTING POWER CABLES: *Rainer Wesche*[1]; Alexander Anghel[1]; Bruno Jakob[1]; Gabriel Pasztor[1]; Georg Vécsey[1]; [1]EPFL, CRPP, c/o Paul Scherrer Institute, WMHA C31, Villigen PSI, AG CH-5232 Switzerland

Superconducting power cables are expected to be one of the most promising energy applications of high-temperature superconductors. The main sources of losses in superconducting cables are ac, dielectric and thermal losses. The interplay of cable geometry, operating current and resulting losses is considered. The design studies indicate that for Ag/Bi-2223 cables with warm dielectric an operating temperature well below 77 K is favourable. The superconductor properties required for the cable application are briefly discussed. Finally, the design concept for a superconducting single-phase transmission cable with a power of 112.5 MW is presented. In 1999 a gas-cooled prototype cable of 5 m length will be constructed and tested in collaboration with Kabelwerke Brugg. Work financially supported by the Swiss Federal Office of Energy and PSEL.

9:10 AM INVITED PAPER

HIGH-T_C SUPERCONDUCTIVITY FOR POWER ENGINEERING - ACTIVITIES AT SIEMENS: *H.-W. Neumüller*[1]; [1]Siemens AG, Corporate Research & Development, P.O. Box 3220, Erlangen, D-91050 Germany

The introduction of superconductivity into electrical power equipment leads to an improvement of existing components i.e. cables, transformers, with respect to smaller size, larger power per unit and better efficiency. Novel components like fault current limiters promise more economic solutions for the distribution and control of power. A very important key role for a successful realisation of HTS-products is played by long-term and secured materials development. Vacuumschmelze Hanau, currently manufactures 2223 BSCCO tape in lengths of 400-600 m having current densities between 22 and 24 KA/cm^2 for use in cables, transformers and magnet windings. Large-area YBCO plate conductors (up to 20x20 cm^2; J_c= 1.5 - 3 MA/cm^2) are under production for the planned 1 MVA Model within our HTS fault current limiter program. Significant progress has been achieved in the field of HTS power cables: a 10 m machine-stranded cable conductor has been successfully tested under A C and DC conditions and a 50 m flexible 100 kV single phase cable is already under construction.

9:30 AM INVITED PAPER

PROGRESS IN Bi-2212 HIGH FIELD INSERT COILS: *Kenneth R. Marken*[1]; Weiming Dai[1]; Huub Weijers[2]; Qingyu Hu[2]; Yusuf Hascicek[2]; Justin Schwartz[2]; [1]Oxford Instruments, 600 Milik St., Carteret, NJ 07008-0429 USA; [2]National High Magnetic Field Lab, 1800 E. Paul Dirac Dr., Tallahassee, FL 32310 USA

Progress has been made toward a goal of adding 3 Tesla in a 20 Tesla background using coils of BiSrCaCuO-2212 tape conductor. The conductor used is a 19 filament tape which has demonstrated short sample current density exceeding 100 kA/cm2 at 4.2 K, 20 T. Double pancake coils were wound in 3 sizes and stacked into concentric sections. A strengthened alloy conductor matrix was used in the outer sections in order to control strains in the higher stress regions of the stack. Individual coil sections, as well as the stacked magnet, will be tested in a 20 T large bore resistive magnet at the NHMFL. Test results and design details will be presented.

9:50 AM INVITED PAPER

RECENT DEVELOPMENT OF HIGH JC Bi-2212/Ag TAPES AND WIRES: *Hitoshi Kitaguchi*[1]; Hanping Miao[1]; Hiroaki Kumakura[1]; Kazumasa Togano[1]; Takayo Hasegawa[2]; Michiya Okada[3]; Jun-ichi Sato[4]; [1]National Research Institute for Metals, 1st Group, 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047 Japan; [2]Showa Electric Wire & Cable Co., Ltd., 2-1-1 Odasakae, Kawasaki, Kanagawa 210-0843 Japan; [3]Hitachi, Ltd., 7-1-1 Ohmika, Hitachi, Ibaraki 319-1292 Japan; [4]Hitachi Cable, Ltd., 3550 Kidamari, Tsuchiura, Ibaraki 300 Japan

Remarkable progress on Bi-2212/Ag conductor fabrication has been achieved recently. Two of newly developed process that enables to obtain high Jc Bi-2212/Ag conductors for practical applications are reported. PAIR process is the combination of pre-annealing (PA) and subsequent intermediate rolling (IR) processes and is performed prior to melt-solidification process. By performing PAIR process, Bi-2212 grain alignment and intergrain connectivity are much improved and a large Jc enhancement can be expected. PAIR processed samples have transport Jc-oxide (4.2 K, 10 T) > 500,000 A/cm2, which corresponds to Jc-conductor of 900 A/mm2 and twice higher than that for the samples melt-solidified without PAIR process. ROSAT (Rotation-Symmetric Arranged Tape-in-tube) wire has been developed. Round wire with small Jc anisotropy can be fabricated with this method. ROSAT wire of 1.6 mm in diameter carries >900 A (4.2K, 0T) which corresponds to Jc-oxide of 250,000 A/cm2 and Jc-conductor of 440 A/mm2.

10:10 AM BREAK

10:20 AM INVITED PAPER

IMPROVEMENT OF FLUX PINNING CENTRES IN MELT PROCESSED Bi-2212/Ag TAPE: *Judith MacManus-Driscoll*[1]; Alice Crossley[1]; David Caplin[1]; [1]Imperial College of Science Technology and Medicine, Centre for High Temperature Superconductivity, Prince Consort Rd., London, England SW7 2BZ 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 $Bi_2Sr_2CaCu_2O_{8+d}$ 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 magnetisation measurements taken in order to assess their effects on pinning within the grains of the Bi-2212. In addition to this, the effect of doping on flux pinning within the grains has been investigated.

10:40 AM INVITED PAPER

MATERIALS ASPECTS REGARDING TO PROCESSING OF BSCCO TAPES: *Peter Majewski*[1]; Andre Aubele[1]; Fritz Aldinger[1]; [1]Max-Planck-Institut für Metallforschung, PML, Heisenbergstr. 5, Stuttgart 70569 Germany

The results of detailed studies of the materials of BSCCO will be presented and discussed in terms of the optimization of the processing. The Ag sheath material of the tapes has been found to dissolve up to 0.3% Cu. This aspect is of great importance for the stoichiometry of the ceramic material, because during processing the Cu content of the ceramic decreases due to diffusion of Cu into the sheath material. The Pb solubility of (Bi,Pb)2+xSr2Ca2Cu3O10+d [(Bi,Pb)2223] has been found to vary significantly with temperature, oxygen partial pressure and presence of silver. This aspect is of great importance for the cooling of the tapes.

11:00 AM INVITED PAPER

HIGH QUALITY HTSC NANOPOWDERS: FABRICATION AND SCALE-UP: Andrei A. Zagorodni[1]; Lingna Wang[1]; Yu Zhang[1]; Kenneth Billqvist[2]; K. Venkat Rao[1]; *Mamoun Muhammed*[1]; [1]Royal Institute of Technology, Mats. Chem. Div., Teknikringen 30, Stockholm 100 44 Sweden; [2]NANOCHEM AB., Stockholm 100 44 Sweden

Since the discovery of HTSC materials, a number of bulk applications have been developed based on their novel properties. Currently, several prototype components and systems are being tested. A major challenge is the availability of high quality powder in large quantities.

The basic requirements of the high quality powders are homogeneity, precise chemical composition, and high reactivity to allow solid-state reactions at short time scales. We report on the development and scale-up of a co-precipitation method for the fabrication of several classes of HTSC nanopowders with exact composition. Large-scale computer-controlled production facility has been constructed. Batches of 3-5 kg powder precursor have been achieved. These nanopowders have been used for the fabrication of Ag-clad tapes with high Jc at very short processing time.

11:20 AM INVITED PAPER

FORECASTING TAPE PERFORMANCE FROM MICROSTRUCTURAL STUDIES IN Ag-CLAD Bi-2223 COMPOSITE CONDUCTORS: Nazarali N. Merchant[1]; *Victor A. Maroni*[1]; Albert K. Fischer[1]; Gilbert N. Riley[2]; Ron D. Parrella[2]; [1]Argonne National Laboratory, CMT, 9700 S. Cass Ave., Argonne, IL 60626 USA; [2]American Superconductor, Two Technology Dr., Westborough, MA 01581-1727 USA

Microstructural studies on transverse sections of mono- and multifilament silver-clad Bi-2223 composite conductors after first stage annealing under optimum conditions have been performed on a variety of wires and tapes over the past several years. We have found a consistent correlation between the microstructures observed by scanning electron microscopy on short anneal samples (quenced in oil) and the final Jc measurements performed on fully processed tapes. Tapes that have microstructures with controlled secondary phase growth and good texture evolution of the layered phase in the early stages of annealing, eventually exhibit high Jcs (50-70 kA/cm2) at 77K and zero field. Conversely, tapes that show extensive secondary phase growth and rapid conversion of the precursor powder to Bi-2223, tend to exhibit poor Jc performance (5-15 kA/cm2). We have also observed that tapes with reproducible conversion kinetics (via XRD), exhibit superior superconducting properties after full processing.

11:40 AM INVITED PAPER

FABRICATION AND CHARACTERISATION OF SUPERCONDUCTING Bi-2223/Ag TAPES WITH HIGH CRITICAL CURRENT DENSITIES IN KM LENGTHS : *Per Vase*[1]; [1]Nordic Superconductor Technologies, Priorparken 878, Broendby, Copenhagen 2605 Denmark

High critical current density, long length Bi-2223/Ag tapes are needed for large scale applications. In this paper we describe our recent result reaching critical current densities of 23 kA/sq.cm and engineering critical current densities of 5.2 kA/sq.cm at 77K over the whole length of the 1250 meters long Bi-2223/Ag tapes. To our knowledge this is the highest critical current density reported for Bi-2223/Ag tapes longer than 1 km. Detailed measurements of the critical current over the 1250 m long tape both by conventional four-probe method and by a specially developed continuous measurement of the remanent field by Hall probes will be reported. Various Ag alloy sheathed Bi-2223 tapes have been made by our standard production line. The approach for improving the homogeneity and the considerations of processing and handling the long length tape will be presented. Electrical, mechanical and thermal properties of our Ag alloy sheathed tapes, including Ag-Au alloy sheathed, will also be described.

HIGH TEMPERATURE COATINGS III: Overlay Coatings for Engine Applications

Sponsored by: Materials Processing and Manufacturing Division, Surface Engineering Committee; Jt. ASM International: Materials Science Critical Technology Sector/TMS Structural Materials Division, Corrosion and Environmental Effects Committee

Program Organizers: Janet Hampikian, Georgia Tech, School of Mats. Sci. & Eng., Atlanta, GA 30332-0245 USA; Narendra B. Dahotre, University of Tennessee Space Institute, Center for Laser Applications, Tullahoma, TN 37388 USA

Tuesday AM Room: 19
March 2, 1999 Location: Convention Center

Session Chairs: John E. Morral, University of Connecticut, Institute of Mats. Sci., Storrs, CT 06268-3136 USA; Christoph Leyens, Oak Ridge National Laboratory, Metals & Ceramics Div., Oak Ridge, TN 37831-6156 USA

8:30 AM INVITED PAPER

SIGNIFICANCE OF BOND COAT OXIDATION FOR THERMAL BARRIER COATING LIFE: *W. J. Quadakkers*[1]; W. Stamm[2]; D. Clemens[1]; L. Singheiser[1]; [1]Forschungszentrum Julich, IWV-2, Julich 52425 FRG; [2]Siemens Power Generation, Mulheim FRG

In modern industrial gas turbines metallic construction materials are protected against the high combustion gas temperatures by yttria stabilized thermal barrier coatings (TBC's). The long term performance of these ceramic coatings requires excellent oxidation properties of the substrate material, because high growth rates and poor adherence of the oxide layers forming during service would lead to early failure of the ceramic TBC. Therefore the high temperature components are protected by an oxidation resistant coating, commonly of the NiCoCrAlY-type prior to applying the TBC. The choice of an optimum NiCoCrAlY bond coat for TBC's not only requires the definition of a suitable NiCoCrAlY composition but also consideration of the multiphase character of the coatings. Changes in phase distribution, determined by coating manufacturing parameters and heat treatment can significantly affect the oxidation properties of the NiCoCrAlY bond coats and consequently TBC life.

8:55 AM

DIFFUSION BARRIERS TO INCREASE THE OXIDATIVE LIFE OF OVERLAY COATINGS: *James A. Nesbitt*[1]; Jih-Fen Lei[2]; [1]NASA Lewis Research Center, Mats. Div., MS 106-1, 21000 Brookpark Rd., Cleveland, OH 44135 USA; [2]Army Research Center, NASA Lewis Research Center, MS 77-1, 21000 Brookpark Rd., Cleveland, OH 44135 USA

Currently, most blades and vanes in the hottest section of aero gas turbine engines require some type of coating for oxidation protection. Newly developed single crystal superalloys have the mechanical potential to operate at even higher component temperatures. However, at these elevated temperatures, coating/substrate interdiffusion can shorten the protective life of the coating. Diffusion barriers between the coating and substrate are being examined to extend the protective life of the coating. A finite-difference diffusion model has been developed to predict the life enhancement due to use of total or partial diffusion barriers. This model simulates Al diffusion to the growing oxide scale as well as into the substrate. Coating failure is predicted when the Al concentration in the coating drops to a critical level. The diffusion model takes into account the reduced interdiffusion between the coating and substrate when a diffusion barrier is present. The diffusion model has been used to predict the effectiveness of diffusion barriers in extending the protective life of a NiAl overlay coating undergoing cyclic oxidation as well as that of a bond coat beneath a ceramic layer (i.e., a

TBC). Experimental results for alumina thin films deposited as diffusion barriers on superalloy substrates will also be presented.

9:15 AM

MICROSTRUCTURES RESULTING FROM COATING/SUPERALLOY INTERDIFFUSION: Fred Meisenkothen[1]; *John E. Morral*[1]; [1]University of Connecticut, Metall. and Mats. Eng., 97 N. Eagleville Rd., Storrs, CT 06269-3136 USA

When coatings and superalloys interdiffuse, there are a variety of microstructures that can form. An example will be given in which small changes in composition of an MCrAlY type coating on a Ni-Cr-Al superalloy can produce the formation of five different microstructures. The microstructures were discovered by combining experimental observations with computer simulations to form an "Interdiffusion Microstructure Map." Such maps can be used in coating design and to predict microstructural changes that will occur during coating service.

9:35 AM

KINETIC CONSIDERATIONS FOR MANUFACTURING A DIFFUSION NiAl COATING UNIFORMLY DOPED WITH A REACTIVE ELEMENT BY CHEMICAL VAPOR DEPOSITION: *W. Y. Lee*[1]; L. He[1]; J. D. Meyer[1]; G. Y. Kim[1]; [1]Stevens Institute of Technology, Dept. of Mats. Sci. and Eng., Castle Point on Hudson, Hoboken, NJ 07030 USA

Recent manufacturing advances in aluminizing by chemical vapor deposition (CVD) offer new processing opportunities to further improve the performance of diffusion NiAl and (Ni,Pt)Al coatings for advanced thermal barrier coating applications. In particular, the dynamic versatility of the CVD aluminzing process provides a potent avenue of uniformly incorporating a reactive element such as Hf in the NiAl coating matrix via proactive control of the concentration of the dopant's precursor in the gas phase. However, with the apparent lack of meaningful experimental data, considerable uncertainties exist to properly project the viability of the doping approach. In this presentation, the critical research issues associated with the doping concept will be discussed with emphasis on generating reliable and reproducible kinetic data and analyzing the kinetics of the doping process.

9:55 AM

ALUMINA/YSZ COMPOSITE COATINGS: D. W. Stollberg[1]; W. B. Carter[1]; *J. M. Hampikian*[1]; [1]Georgia Institute of Technology, School of Mats. Sci. and Eng., 778 Atlantic Dr., Atlanta, GA 30332-0245 USA

Multi component coatings of alumina and yttria stabilized zirconia (YSZ) containing from zero percent alumina up to the eutectic composition have been deposited via liquid fuel combustion chemical vapor deposition (CVD) onto single crystal sapphire substrates. Aluminum acetylacetonate, and 2-ethylhexanoates of yttrium and zirconia were used as chemical coating precursors dissolved in toluene. The coatings will be incorporated into thermal barrier coatings (TBCs) as an interlayer between the metallic bond coat and the ceramic top coat in an effort to strengthen the bond coat/ceramic interface as measured by thermal fatigue testing. Nanoindentation measurements of the hardness and fracture toughness of the alumina/YSZ coatings will be reported.

10:15 AM BREAK

10:35 AM INVITED PAPER

HIGH ASPECT RATIO MICROSTRUCTURE- SUPPORTED SHROUD FOR A TURBINE BLADE: *K. W. Kelly*[1]; [1]Louisianna State University, Mech. Eng. Dept., 2502 CEBA, Baton Rouge, LA 70803 USA

A major component in the development of advanced gas turbine engines is the increase of turbine inlet temperatures. Associated with this drive for higher turbine inlet temperatures is the need for more effective blade cooling strategies. Current cooling technology relies primarily on a combination of internal cooling through serpentine ribbed-coolant passages that are integrally cast in the blades or film cooling where a coolant jet is injected through a series of coolant holes on the blade surfaces. In the proposed research, a new concept of significantly increasing turbine-blade heat transfer is proposed, and is based on electrodepositing a moderately dense array of microstructures (nickel or nickel-alloy) directly on the blade surface with a nickel-alloy shroud on top. Preliminary results, resulting from an ongoing research program at LSU funded by the Defense Advanced Research Project Agency (DARPA), have already demonstrated the feasibility of this approach. The manufacturing process to build this shroud will be described and the results from heat transfer tests which quantify its performance will be provided.

11:00 AM

EFFECTS OF PLATINUM ADDITIONS AND SULFUR CONTENT ON THE ADHESION OF ALUMINA SCALES TO CVD ALUMINIDE BOND COATS: *J. Allen Haynes*[1]; Ying Zhang[2]; Woo Y. Lee[3]; Bruce A. Pint[1]; Ian G. Wright[1]; Peter K. Liaw[2]; [1]Oak Ridge National Laboratory, P.O. Box 2008, M.S. 6063, Oak Ridge, TN 37831-6063 USA; [2]University of Tennessee, School of Eng., Knoxville, TN USA; [3]Stevens Institute of Technology, Castle Point on Hudson, Hoboken, NJ USA

The adhesion of alumina scales to aluminide bond coats is the life-limiting factor for some advanced thermal barrier coating systems. It has been demonstrated that scale adhesion on superalloys can be substantially improved by reducing S impurities; and scale adhesion on aluminide coatings is enhanced by Pt additions. This work investigated the effects of aluminide bond coat sulfur and platinum contents on alumina scale adhesion. Low-sulfur NiAl and NiPtAl bond coats were fabricated by aluminizing de-sulfurized René N5 using a unique low-sulfur chemical vapor deposition (CVD) process. Scale adhesion was investigated by isothermal and cyclic oxidation testing at 1150°C. Lowering the sulfur content of CVD NiAl significantly improved scale adhesion, but scale spallation eventually initiated along coating grain boundaries. Significant improvements in scale adhesion along bond coat grain boundaries were obtained after Pt additions, although sulfur levels were higher in CVD NiPtAl due to impurities in the electroplated Pt. The observed influences of Pt additions included (1) considerable reductions in scale-metal void growth, and (2) reductions in Ta-rich oxides in the scales above the bond coat grain boundaries. The influence of bond coat microstructure on scale adhesion will also be discussed.

11:20 AM

THERMOMECHANICAL FATIGUE OF A SINGLE CRYSTAL SUPERALLOY: INFLUENCE OF A PROTECTIVE COATING: *Alejandro Sanz*[1]; L. Llanes[3]; J.-P. Bernadou[2]; M. Anglada[3]; [1]Danieli Research and Development, Mats. Development, Via Nazionale 41, Buttrio 33042 Italy; [2]E.N.S.A.E., Laboratoire de Metallurgie, 10 Av. E. Belin, Toulouse, Cedex 31055 France; [3]U.P.C., ETSII, Depto. de Ciencia de Los Materiales y Metalurgia Av, Diagonal 647, Barcelona, 08028 Spain

The improvement of the gas turbine engine efficiency requires to have the highest possible Turbine Inlet Temperature (T.I.T.). Turbine's turbine blades and nozzle vanes are commonly protected against high temperature degradation with NiCoCrAlYTa coatings. A careful selection of the coating which offers sufficient chemical compatibility with the substrate and a low interdiffusivity is necessary for these high temperature systems. AM-3 single-crystals, [001] oriented, coated with a Low Pressure Plasma Spray (LPPS) NiCoArAlYTa coating were submitted to thermomechanical fatigue conditions until fracture. The thermomechanical fatigue test consisted of strain controlled cycle having four slopes and a duration of 180 seconds. The temperature range extended from 923ϒK (650ϒC) to 1373ϒK (1100ϒC). Two strain ranges of $\Delta\varepsilon_{max}/2$=0.5% and $\Delta\varepsilon_{max}/2$=0.25% were chosen for this study. This cycle schematically reproduces the strain evolution of the leading edge, blade's critical element in a civil turbine engine under normal working conditions. Using the data obtained from Energy Dispersive microprobe Spectroscopy (EDS) the diffusional phenomena between the coating and the substrate is characterised and correlated with the stress gradient and test temperature. Scanning Electron Microscopy (SEM) analysis were performed at each condition to establish the fracture mechanisms and the microstructural evolution, correlationing them to the presence of a NiCoCrAlYTa protective coating.

11:40 AM

REACTIVE PROCESSING OF A DENSE FUNCTIONALLY-GRADED INTERMETALLIC MATRIX COMPOSITE COATING: *Hexiang Zhu*[1]; Reza Abbaschian[1]; [1]University of Florida, Dept. of Mats. Sci. and Eng., 224 MAE, P.O.Box 116400, Gainesville, FL 32611 USA

A dense functionally-graded intermetallic matrix composite (FGIMC) coating on NiAl substrate has been successfully fabricated by reactive hot compaction technique. The FGIMC coating consisted of four NiAl/Al_2O_3 composite layers with alumina content varying from less than 3 vol.% to about 36 vol.%, with thickness of about 900μm. The microstructures of the coating and microhardness profiles across its thickness were characterized and compared to those of a one-layer NiAl -36 vol%Al_2O_3 composite coating on NiAl substrate. The comparison indicated that the bonding between FGIMC coating and NiAl substrate was stronger than that between single NiAl-36 vol.%Al_2O_3 composite coating and NiAl substrate. This is attributed to the reduction in residual stresses resulting from the more gradual composition transition in FGIMC coating.

HUME ROTHERY SYMPOSIUM TO HONOR M. HILLERT; ALLOY EFFECTS ON MIGRATING INTERFACES: Session II

Sponsored by: Jt. Electronic, Magnetic & Photonic Materials Division/Structural Materials Division, Alloy Phases Committee; ASM International: Materials Science Critical Technology Sector,Thermodynamic Activities & Phase Equilibria Committee
Program Organizers: Y. Austin Chang, University of Wisconsin, Dept. of Mats. Sci. and Eng., Madison, WI 53706-1595 USA; Ray Y. Lin, University of Cincinnati, Dept. of Mats. Sci. & Eng., Cincinnati, OH 45221-0012 USA

Tuesday AM Room: 14A
March 2, 1999 Location: Convention Center

Session Chairs: W. J. Boettinger, NIST Metallurgy Division, Gaithersburg, MD 20899 USA; R. Y. Lin, University of Cincinnati, Dept. of Mats. Sci. and Eng., Cincinnati, OH 45221-0012 USA

8:30 AM INVITED PAPER
MOTION BY CURVATURE AND IMPURITY DRAG: *J. W. Cahn*[1]; Amy Novick-Cohn[2]; [1]NIST, Mats. Sci. and Eng. Laboratory, Gaithersburg, MD 20899 USA; [2]Technion-IIT, Dept. of Mathematics, Haifa 32000 Israel

Diffuse interfaces between ordered domains (APB) provide a good testing ground for ideas about the interactions of solutes with moving interfaces. The free energy, thickness, and amount of adsorption can be manipulated experimentally over many orders of magnitude near critical temperatures for order-disorder transitions. Motion of such interfaces is by atomic diffusion on a common lattice, and does not require long range diffusion. We present a system of equations to model this diffusive motion and obtain a single equation for the predicted velocity that contains many factors. Interface motion is by curvature, and the velocity of motion is linear in surface free energy. However, this surface free energy factor is canceled by a term in the mobility in the limit of no adsorption, and the velocity of motion is approximately independent of the interfacial free energy and reduces to the result of Allen and Cahn. Adsorption lowers the velocity by a term that mimics what is expected for impurity drag. Near wetting transition with thick wetting layers the velocity becomes inversely proportional to their thickness. We examine the predictions near the tricritical point, and compare the results with experiments.

9:10 AM INVITED PAPER
THE THERMODYNAMICS OF INTERFACES FAR FROM EQUILIBRIUM: *Peter W. Voorhees*[1]; [1]Northwestern University, Dept. of Mats. Sci. and Eng., 2225 N. Campus Dr., Evanston, IL 60208 USA

A general thermodynamical description of an evolving interface appropriate to situations far from equilibrium is developed. The theory represents a departure from theories based on classical nonequilibrium thermodynamics as we do not assume a linear relation between fluxes and forces, and we do not limit our theory to small departures from equilibrium. Two examples of this approach will be presented. The first deals with the effects of diffusion in the bulk phases, solute drag and interfacial diffusion on the thermodynamics of the interface. In the second the conditions setting the velocity of the facets that compose a fully faceted interface in an elastically stressed solid are derived. We find, for example, that the singularities in the elastic stress induced by the presence of corners do not influence the velocity of a facet.

9:50 AM BREAK

10:00 AM INVITED PAPER
PHASE FIELD MODELING OF ALLOY SOLIDIFICATION: *James A. Warren*[1]; *William J. Boettinger*[1]; [1]NIST, Metall. Division, Bldg 223/B164, Gaithersburg, MD 20899 USA

The phase field method has been used with considerable success over the past five years to model solidification phenomena. This method starts from thermodynamic principles employing gradient energies and adds reasonable kinetic postulates to yield differential equations that govern the evolution of the solidification microstructure, without explicitly tracking the interface position. These equations can, under appropriate initial conditions, describe processes such as solute trapping, solute drag, Mullins-Sekerka instabilities, cellular/dendritic growth, and dendrite sidearm coarsening, fragmentation and bridging. The microsegregation patterns associated with these phenomena can be predicted and characterized. Both two and three dimensional simulations will be discussed. A recent modification of the approach permits the modeling of the solidification of grains with different orientations.

10:40 AM INVITED PAPER
SOLUTE DRAG IN ALLOY SOLIDIFICATION: *Michael J. Aziz*[1]; [1]Harvard University, Div. Eng. & Applied Sci., 29 Oxford St., Cambridge, MA 02138 USA

Several models for the kinetics of interface motion in binary alloys are based on the pioneering work of Hillert and Sundman. Some find a solute drag effect, as suggested by Hillert and Sundman for the migration of interphase boundaries, whereas others have not. Some of these models have been applied to binary alloy solidification and tested experimentally. The implications of the experimental results for kinetic models of interface motion will be discussed.

INTERCONNECTPACK; INTERCONNECTIONS FOR ELECTRONICS PACKAGING: Interfacial Reaction

Sponsored by: Electronic, Magnetic & Photonic Materials Division, Electronic Packaging & Interconnection Materials Committee
Program Organizers: Gautam Ghosh, Northwestern University, Dept. of Mats. Sci., Evanston, IL 60208-3108 USA; Sung Kang, IBM, TJ Watson Research Center, Yorktown Heights, NY 10598 USA; Rao Mahidhara, Cypress Semiconductor Corp, San Jose, CA 95134 USA; Ephraim Suhir, Bell Labs., Murray Hill, NJ 07974 USA

Tuesday AM Room: 17A
March 2, 1999 Location: Convention Center

Session Chairs: K. N. Tu, University of California, Dept. of Mats. Sci. and Eng., Los Angeles, CA 90095, USA; K. N. Subramanian, Michigan State University, Dept. of Mats. Sci. and Mech., East Lansing, MI 48824-1226 USA

8:30 AM INVITED PAPER
AN IMPROVED NUMERICAL METHOD FOR PREDICTING INTERMETALLIC LAYER THICKNESS DEVELOPED DURING THE

FORMATION OF SOLDER JOINTS ON Cu SUBSTRATES: S. Chada[1]; *R. A. Fournelle*[1]; D. Shangguan[2]; [1]Marquette University, Mats. Sci. Program, P.O. Box 1881, Milwaukee, WI 53201-1881 USA; [2]Ford Motor Company, Visteon Automotive Systems, 17000 Rotunda Drive, Dearborn, MI 48121 USA

An improved numerical method has been developed for calculating the thickness of intermetallic layers formed between Cu substrates and solders during the soldering process. The improved method takes into account intermetallic dissolution during heating and intermetallic precipitation during cooling and requires as input (1) the temperature-time profile for the soldering process, (2) the experimentally determined isothermal growth parameters for the growth of the intermetallic layer into Cu saturated molten solder, (3) the experimentally determined Nernst-Brunner parameters for the dissolution of Cu into molten solder, (4) the experimentally determined solubility of Cu in molten solder and (5) assumptions about the thickness of the boundary layer in the liquid ahead of the growing intermetallic. Calculations show that the improved method predicts intermetallic growth between Cu substrates and 96.5Sn-3.5Ag and 62Sn-36Pb-2Ag solders during reflow soldering better than a previously developed method, which did not take into account dissolution during heating and precipitation during cooling. Calculations further show that dissolution has a significant effect on intermetallic growth, while precipitation does not.

8:55 AM INVITED PAPER

INTERFACIAL REACTIONS IN THE Ag-Sn/Cu COUPLES: Yee-wen Chen[1]; *Sinn-wen Chen*[1]; [1]National Tsing-Hua University, Dept. of Chem. Eng., Kuang-Fu Rd., Hsinchu 30043 Taiwan

Two types of diffusion couples, Sn-3.5 wt.%Ag/Cu and Sn-25.0 wt.%Ag/Cu, have been studied. The phases formed at the interfaces and their thickness have been examined. The reaction temperatures were at 240°C and 450°C, and the reaction time varied from 5 minutes to 72 hours. At 240°C, only Cu_3Sn and Cu_6Sn_5 phases are formed. At 450°C, Cu_4Sn, Cu_3Sn, and Cu_6Sn_5 phases formed in the Sn-3.5 wt.%Ag/Cu couple; while Cu_4Sn, Cu_3Sn, Cu_6Sn_5, and Ag_3Sn phases formed in the Sn-25 wt.%Ag/Cu couple. The interfaces between the molten solder and the solid intermetallic phases had a wavy morphology; while those between the solid intermetallic phases and the solid Cu substrate were relatively planar. The isothermal sections of the Ag-Sn-Cu system at 240°C and 450°C have been assessed. The interfacial reaction paths are proposed. It is concluded that the Cu_6Sn_5 and Ag_3Sn phases formed during solidification not by interfacial reactions.

9:20 AM

INTERFACIAL REACTION BETWEEN Ni, Pd and Sn-Bi AND Sn-Ag EUTECTIC SOLDERS: *G. Ghosh*[1]; [1]Northwestern University, Dept. of Mats. Sci. and Eng., 2225 N. Campus Dr., Evanston, IL 60208-3108 USA

Metallization schemes using Ni and Pd are becoming increasingly popular in electronic packaging. Both two-layer and four-layer Ni-Pd coatings are being used for soldering of various components using Pb-Sn solders. However, there is a growing interest in the use Pb-free solders. This paper deals with a systematic study of interfacial reaction between bulk Ni and Pd substrates and Sn-Bi and Sn-Ag eutectic solders. The evolution of interfacial microstructures due to both liquid- and solid-state reactions will be presented. The products of interfacial reaction are characterized by SEM, TEM and AEM. The microstructural evolution at the interface and the diffusion path will be discussed in terms of the calculated isothermal sections of the corresponding ternary system at the experimental temperature of interest.

9:40 AM

CHARACTERIZATION OF THE GROWTH OF INTERMETALLIC INTERFACIAL LAYERS OF Sn-Ag and Sn-Pb EUTECTIC SOLDERS AND THEIR COMPOSITE SOLDERS ON Cu SUBSTRATE DURING ISOTHERMAL LONG-TERM AGING: *S. Choi*[1]; T. R. Bieler[1]; K. N. Subramanian[1]; [1]Michigan State University, Mats. Sci. & Mech., Eng. Bldg. # 3536, East Lansing, MI 48824-1226 USA

The intermetallic layer formation between solder and substrate indicates a firm bonding of solder material with substrate. However, the solid state growth of intermetallic interfacial layers have been known to adversely affect the mechanical properties and reliability of solder joints, leading to fracture at or near the interfacial layer. Single shear lap joints were made with four different solders, Sn-Pb and Sn-Ag eutectic solders, and their composites containing about 20 vol% in-situ Cu_6Sn_5 intermetallic phases about 3-8 micrometers in diameter. Two sets of experiments were performed: First, all of the above four solder joints were aged at 150°C for periods ranging to 4000 hours and the intermetallic growth was monitored periodically. Second, each of the above four solder joints was aged at five different temperatures for 4000 hours. The interfacial layers between solders and the Cu substrate were examined using optical microscopy and scanning electron microscopy. The kinetics of growth of intermetallic interfacial layers formed between solders and Cu substrate was characterized. Effects of in-situ Cu_6Sn_5 intermetallic phases on the growth rate were also characterized. The intermetallic layers grew much slower in the composite solders for the first 350 hours for the Sn-Pb composite and for the first 1200 hours for the Sn-Ag composite as compared to the corresponding non-composite solders. Thereafter, the growth rates were more similar, and the thickness became nominally similar in the 150ϒC specimen after about 4000 hours, when the reinforcements were also quite large.

10:00 AM INVITED PAPER

Pb-FREE SURFACE-FINISH ON ELECTRONIC COMPONENT TERMINALS FOR Pb-FREE SOLDER ASSEMBLY: H. Tanaka[1]; M. Tanimoto[1]; A. Matsuda[1]; *S. Shiga*[1]; [1]Furukawa Electric Co., Ltd., R&D Division, Metal Research Center, 500 Kiyotaki, Nikko 321-0942 Japan

Terminals of electronic components such as IC's, connectors and condensors are presently surface-finished with Sn-Pb alloys in general in order to keep solderability without Sn-whisker occurrence. NCMS's Pb-free Solder Project reports that Sn-Pb alloys have some disastrous effects on the melting behaviors in case of Pb-free solder assembly, some of which are due to the formation of low melting phases that may generate when Pb-free solders with Bi and/or In are mixed with Sn-Pb coatings. In the final report published in Aug. 1997, written is that the much larger topic of eliminating Pb from solderable surface finishes will need to be addressed before Pb-free alloys are implemented. In Japan, developed were two types of Pb-free solderable finishes, one of which is simple Ni/Pd double layer mostly IC lead frames, while Au-flash can be top-coated in order to enhance solderability. Although showing a variety of benefits, both technical and economical, this system have some retarding aspects of Pd's supply and price situation along with hazardous corrosion characteristics in case of its application to ferrous base metals such as Fe-Ni alloys. Different from the precious metal system, the second system consists of two layers, thicker Sn underlayer and thin Sn-Bi alloy over layer, which are electroplated in succession. In comparison with the monolayer of Sn-Bi which reacts hazardously with base metals such as copper, this double layer system shows superior performances similar to the conventional Sn-Pb with regard to wetting time and temperature, shelf life of solderability, whisker occurrence and so on. This is due to the surface localization of a small amount of Bi. Along with diffusion rates and metallographies, some practical usages and related data will be presented.

10:25 AM BREAK

10:40 AM INVITED PAPER

INTERACTION BETWEEN COPPER AND AN EUTECTIC Pb-Sn/HIGH Pb COMPOSITE SOLDER FOR MICROELECTRONIC PACKAGING : *A. S. Zuruzi*[1]; C. Chiu[1]; K. M. Chua[2]; W. T. Chen[1]; S. K. Lahiri[1]; [1]National University of Singapore, Microelectronics Materials, Processes and Packaging Programme, Blk S7, Level 3 119 260 Singapore; [2]Gintic Institute of Manufacturing Technology, 71 Nanyang Dr. Singapore

Use of composite solders comprising eutectic Pb-Sn and higher lead solders is an option for joining chips to substrates at lower temperatures. In this work the reaction between such composite solders and copper, which results in Cu-Sn intermetallic compound formation, during solder reflow processes was investigated for both flip chip and BGA types of applications. The thickness of the intermetallic compound was found to increase with the square root of the number of reflows, which suggests that the compound growth is dominated by a diffusion controlled mechanism. This result is similar to observations made in constant temperature annealing studies. The similarity leads to a simple method to assess

how the compound growth rate is affected by the temperature-time profile.

11:05 AM
DISSOLUTION AND REACTION KINETICS OF THE SOLDER-BALL PADS IN BGA DURING REFLOW SOLDERING: *C. R. Kao*[1]; J. A. Ho[1]; [1]National Central University, Dept. of Chem. Eng., Chungli Taiwan

The solder-ball pads in a Ball-Grid-Array (BGA) package are made up of several metal layers. The Au/Ni/Cu tri-layer structure is the most common pad metallization. In this structure, the first layer which is to be in direct contact with solder is the Au layer, which has a thickness of about 1 micron. Below this Au layer is the Ni layer, whose thickness is about 3 microns. The Cu layer is part of the internal wiring within the BGA package, and its thickness is often greater than 20 microns. During reflow soldering, the Au layer dissolves into the solder rather quickly, and the Ni layer is then exposed to the solder. In this study, we report the dissolution kinetics of the Au layer and the reaction kinetics of Ni layer with solder in commercial BGA substrates. The spatial distribution of the dissolved Au atoms in solder is also determined. These information are helpful in determining the optimal reflow temperature profile.

11:25 AM
INTERFACIAL MICROSTRUCTURE EVOLUTION OF Pb-Sn SOLDER JOINTS ON Ni/Pd/Cu METALLIZATIONS: *G. Ghosh*[1]; [1]Northwestern University, Dept. Mats. Sci. and Eng., 2225 N.Campus Dr., Evanston, IL USA 60208-3108

This paper will examine the interfacial microstructure of the Pb-Sn solder joints on Ni/Pd/Cu metallizations. Both liquid-state and solid-state reactions have been investigated using the eutectic (62Sn38Pb) and a high-lead (95Pb5Sn) solders. A two-layer (Pd/Ni) and a four-layer (Pd/Ni/ni-Pd/Ni) metallization schemes on Cu are used as substrates. The interfacial microstructures have been characterized using a variety of electron microscopy techniques, such as SEM, TEM and AEM. The formation of voids at interface and the complex interfacial microstructures due to interdiffusion and phase transformation will be discussed in detail.

11:45 AM
ANALYSIS OF THE UPPER PEAK OF WETTING FORCE-TIME CURVE USING Sn-37Pb, Sn-3.5Ag SOLDERS: *Jae Yong Park*[1]; Jae Pil Jung[2]; Choon Sik Kang[1]; [1]Seoul National University, Dept. of Mats. Sci. and Eng., San 56-1, Shillim-dong, Kwanak-Ku, Seoul 151-742 Korea; [2]University of Seoul, Dept. of Mats. Sci. and Eng., 90, Jeonnong-dong, Dondaemun-Ku, Seoul 130-743 Korea

The meniscograph/wetting curve is a very useful tool for quantifying the wettability of solder, but its meaning and mechanism have not been fully developed yet, especially the upper peak of the wetting curve which can be shown when Cu plate is detached from solder bath. To evaluate this peak, two kinds of experiments were performed: 1) Cu plates from which two adjacent corners are cut out in various sizes of squares were used to compare with the regular rectangular Cu plate; 2) the immersion depth of the regular rectangular Cu plate to be dipped into solder bath varied from 0.5mm to 9.5mm. Sn-37Pb and Sn-3.5Ag solders were used for both experiments. In the case of the first experiment using cut out plates, the upper peak of the wetting curve changed to a rather round shape and a very short horizontal segment appeared after the peak, followed by a downfall. This horizontal segment represents the point of transition where the sliding solder reached the edge of the cut out Cu plate. According to the second experiment, the amount of time needed for the curve to reach the peak increases in proportion to the immersion depth of Cu plate while the span of time taken for the drop of the curve remained independent of the depth. The force value on the horizontally steady line of the wetting curve was inversely proportional to the immersion depth while the force value on the pinnacle of the upper peak remained constant. This means that the latter is influenced by the buoyancy force while the former is not. It can be concluded from the results that: (1) ascending segment of the upper peak represents the sliding of solder on Cu plate; (2) the pinnacle of the upper peak stands for the state in which the sliding solder meets the edge of the Cu plate.

INTERNATIONAL SYMPOSIUM ON ADVANCES IN TWINNING: Twinning in Electronic Materials

Sponsored by: Structural Materials Division, Physical Metallurgy Committee

Program Organizers: S. Ankem, University of Maryland, Dept. of Mat. & Nuclear Eng., College Park, MD 20742-2115 USA; Chandra Pande, Naval Research Lab, Mats. Sci. & Tech. Div., Washington, D.C. 20375-5000 USA

Tuesday AM — Room: 17B
March 2, 1999 — Location: Convention Center

Session Chairs: Bhakta B. Rath, Naval Research Laboratory, MS & CT Directorate, Washington, D.C. 20375-5320 USA; David O. Welch, Brookhaven National Laboratory, Mats. Sci. Div., P.O. Box 5000, NY 11973-5000 USA

8:30 AM INVITED PAPER
STACKING FAULTS AND TWIN GENERATED ANTI PHASE DOMAINS IN SEMICONDUCTOR HETEROSTRUCTURES: *Aristos Christou*[1]; [1]University of Maryland, Dept. of Mats. and Nuclear Eng., Bldg. 090, Room 2135, Stadium Dr., College Park, MD 20742-2115 USA

The formation of antiphase domains may be ideally investigated through the growth of a polar on non-polar semiconductor such as GaAs on silicon. Such investigations have been carried out and we now have a clear model on the generation of APD as a function of interfacial strain at the interfaces of such semiconductors. Through transmission electron microscopy, initial misfit strain is usually accommodated through the generated or initiated at stacking faults or twins which proceed to enlarge as the growth process continues. The APB boundary is therefore a twinned of SF boundary leading to eventual three dimensional growth. We have isolated single SF randomly distributed and not at all affected by the distribution of misfit dislocations. These SF grow into twin boundaries as the growth process continues and are affected directly by the specific growth conditions. Electrically, film mobility is greatly reduced due to the presence of APDs, and the degree of reduction depends on compensating impurities. Twins in lattice matched heterosystems are also presented. In such samples, twins are always initiated at growth abnormalities close to the interfaces of systems such as the InGaAs/InP configuration. The twin density may be affected again by growth kinetics.

9:05 AM INVITED PAPER
THE PHENOMENOLOGY AND THERMODYNAMICS OF THE STRUCTURE OF TWINS AND TWIN BOUNDARIES IN $YBa_2Cu_3O_x$ SUPERCONDUCTORS*: *David O. Welch*[1]; [1]Brookhaven National Laboratory, Mats. Sci. Division, Bldg. 480, P.O. Box 5000, Upton, NY 11973-5000 USA

Twins and twin boundaries play some important roles in the high-T_c superconductor $YBa_2Cu_3O_x$. Among other things, twin boundaries serve as pinning centers for magnetic flux and as diffusion paths for oxygen. The organization of the twin structure serves to relieve elastic strain in confined microstructures such as in superconducting films on substrates and in composite conductors. In this paper, I will review what is known about the local atomic structure and composition of twin boundaries and their dependence on oxygen content and alloying additions, together with the systematics of the dependence of twin density on grain size, oxygen content, and alloying additions. I will then discuss thermodynamic and atomistic models which can be used to describe the compositional and strain distributions near twin boundaries, as well as their effect on the density of electronic holes, which plays a vital role in several superconducting properties. *This research was supported by the U.S.

Department of Energy, Division of Materials Sciences, Office of Basic Energy Sciences under Contract No. DE-AC02-98CH10886.

9:40 AM INVITED PAPER

TWINNING IN $YBa_2Cu_3O_{7-x}$ SUPERCONDUCTORS: *Yimei Zhu*[1]; [1]Brookhaven National Laboratory, Dept. of Applied Sci., Bldg. 480, Upton, NY 11790 USA

The most prominent structural defects in YBa2Cu3O7-x (x<0.5) are twins. Below about 750ϒC, YBa2Cu3O7-x undergoes a tetragonal-to-orthorhombic structural phase transition, resulting in twinning on the {110} planes. Twins are formed to reduce strain energy due to the change in shape and volume resulting from the phase transformation. The spacing of the twin lamella is determined by minimizing the total energy associated with the strain energy at the grain boundaries where the twins terminate and the interfacial energy of the twin boundary. High-resolution electron microscopy and electron energy-loss spectroscopy studies suggest that there are two types of twin boundaries in YBa2Cu3O7-x: one with a lattice translation (~d110) along the boundary for fully oxygenated samples (x~0.0), and the other, without a lattice translation, for oxygen-deficient ones. Electron diffraction and fringe analysis of the twin boundaries show that the former is an alpha-delta interface, while the latter is a pure delta-inter face. In-situ experiments indicate that the structure of the twin boundaries can change from one type to the other. This structural transition was analyzed using the observed twinning dislocations and steps within the framework of a modified coincidence-site-lattice model. Work supported by the U.S. DOE DE-AC02-98CH10886.

10:15 AM BREAK

10:25 AM INVITED PAPER

DOMAINS IN FERROELECTRIC THIN FILMS AND HETERO-STRUCTURES: *Ramamoorthy Ramesh*[1]; [1]University of Maryland, Dept. of Mats. and Nuclear Eng., Bldg. 090, Rm. 2135, Stadium Dr., College Park, MD 20742-2115 USA

Ferroelectric materials undergo a phase transition from the paraelectric (high temperature) to the ferroelectric (low temperature) phase, accompanied by a change in crystal structure and symmetry. The strain accompanying these structural and electric phase transformations is generally accommodated by the formation of domains, that are separated by domain walls. Due to the fact that the anisotropy in these materials is rather high and the exchange interaction rather weak, these domain walls are very thin (of the order of a few atomic spacings). A typical case is that of the cubic-tetragonal transformation in the lead zirconate titanate (PZT) system, accompanied by the formation of 90 degree domains. Domain wall in ferroelectrics can move under the influence of electric or stress fields (ferroelastic). Since these domain walls can exist in thin films of ferroelectric materials, that are likely to be used in non-volitale memories, piezoelectric actuators and pyroelectric sensors, it is important to understand the statics and dynamics of domain evolution in them. In these presentation, I will review some of the work on-going in our program that is aimed at establishing the structure-property-processing interrelationships relevant to domain formation in ferroelectric thin films.

11:00 AM

RELAXATION OF COHERENCY STRAIN VIA TWINNING IN Ge-C AND Ge-Si-C EPITAXIAL THIN FILMS: *Mohan Krishnamurthy*[1]; Bi-Ke Yang[2]; *Jong K. Lee*[1]; [1]Michigan Technological University, Metall. and Mats. Eng., 1400 Townsend Dr., Houghton, MI 49931 USA; [2]IRF, Inc., Temecula, CA USA

In thin films, plastic relaxation of coherency strain due to a lattice mismatch is accommodated typically by misfitting and/or threading dislocations. There is, however, a strong indication that coherency strain is also relaxed through twinning in Ge1-xCx and Ge0.8-xSi0.2Cx (nominal x < 0.1) films grown epitaxially on Si(100) subatrates. Low temperature (~200ϒC) molecular beam epitaxy can engineer the immiscible Ge-C system to form a dilute binary with substitutional C fractions typically ~ 1-2 atomic%. X-ray and transmission electron microscopy analyses of such epitaxial films indicates that the presence of C diminishes the role of dislocations and increases the tendency for the formation of stacking faults and twins. The density of twins increases with increasing C concentrations and, in the case of GeSiC films, increasing Si fractions. Details of the experimental results as well as a theoretical model based on the discrete atom method will be discussed for the role of twinning in such epitaxial thin films.

INTERNATIONAL SYMPOSIUM ON GAMMA TITANIUM ALUMINIDES: TiAl Alloys: Alloys and Properties

Sponsored by: Structural Materials Division,Titanium Committee, Structural Materials Committee; ASM International: Materials Science Critical Technology Sector, Materials Synthesis & Processing

Program Organizers: Young-Won Kim, UES, Inc., Mats. & Proc. Div, Dayton, OH 45432-1805 USA; Dennis M. Dimiduk, Wright-Patterson AFB, WL/MD, WPAFB, OH 45433 USA; Michael H. Loretto, University of Birmingham, IRC, Birmingham B15 2TT UK

Tuesday AM Room: 8
March 2, 1999 Location: Convention Center

Session Chairs: MIchael H. Loretto, The University of Birmingham, IRC, Birmingahm, West Midlands B15 2TT UK; Donald L. Anton, United Technologies Research Center, MS-129-22, 411 Silver Lane, East Hartford CT 06108 USA

8:30 AM INVITED PAPER

ALLOY AND PROCESS IMPROVEMENTS FOR CAST GAMMA TIAL ALLOY APPLICATIONS: *Paul A. McQuay*[1]; [1]Howmet Research Corporation, Advanced Technology, 1500 South Warner St., Whitehall, MI 49461-1895 USA

Recent cast alloy development efforts have focused on the improvement of creep resistance through alloying and micro-alloying additions. Specifically, micro-alloying additions of carbon have been shown to reduce the time to 0.2% primary creep strain by up to an order of magnitude, while only slightly reducing the room temperature ductility. Additionally, the Howmet Corporation has developed several net or near-net shape casting processes which produce components which meet industry requirements for metallurgical integrity and performance. Using these processes, component development efforts have focused on diesel engine turbocharger wheels, and small structural and airfoil components for turbine engines. The status of these manufacturing technologies, microstructure and property relationships of selected alloys, and examples of near-term production opportunities will be reviewed and discussed.

9:00 AM

STUDY OF MICROSTRUCTURE TO IMPROVE CREEP PROPERTIES OF CAST TiAl-Fe-V-B ALLOY: *Sadao Nishikiori*[1]; Kenji Matsuda[1]; [1]Ishikawajima-Harima Heavy Industries Co., Ltd., Mat. Tech. Dept., 3-1-15, Kotou-ku, Tokyo 135 Japan

A gamma titanium aluminide, Ti-46.7Al-Fe-V-B with duplex structure, has been developed as a casting material for high temperature structural use in aero-engines. This alloy is characterized by the addition of Fe and V which improve castability. In order to apply this alloy to various rotating parts operated at temperatures up to 750ϒC, further improvements of creep strength will be required. In general, it is widely known that lamella structure, coarse grains and/or increase of degree of serration at grain boundaries have the advantage of improving the creep strength. So, viewed in these metallographical behavior, the possibility of modifying microstructure in TiAl-Fe-V-B system was investigated. Then, as compared with creep properties results, effects of alloying elements and heat treatment process were estimated with metallografic characterization.

9:20 AM

MECHANISMS OF LAMELLAR REFINEMENT DURING PRIMARY CREEP OF NEAR - GAMMA DUPLEX TiAl: *Thomas R. Bieler*[1]; Dong Yi Seo[1]; [1]Michigan State University, Dept. of Mats. Sci. and Eng., 3536 Eng. Bldg., East Lansing, MI 48824-1226 USA

Primary creep has been measured in a number of near-gamma TiAl alloys with duplex microstructures. Two stages of primary creep deformation occur, an early and rapid process that exhausts itself after about 0.2-0.5% strain, and a different process that dominates the deformation up through the minimum creep rate. When creep data are fit to functions that are complex enough to accurately represent the measured strain-time data, these two stages are easily observed in a strain-rate vs. strain (or time) plot. From interrupted creep tests, the early process causes lamellar refinement, i.e. a reduction in lamellar spacing, and the second process does not alter the lamellar spacing significantly. The primary creep resistance is dominated by the rate at which the early process is exhausted. Since lamellar refinement is a metric of this early process, simulations of the refinement process have been made to examine possible mechanisms that could account for the observed refinement. The simulation is made by starting with a set of lamellar spacings that represent the undeformed lamellar spacing frequency distribution. The thickest lamellae are subdivided in a manner that changes the frequency distribution to match the deformed distribution by assuming that twins and/or strain induced gamma-alpha2 phase transformations occur parallel to lamellar planes. The effects of lamellar spacing bin size, and the relative fractions of twinning or gamma-alpha2 shear transformations are examined to consider how different deformation histories affect the resulting deformed distribution, and the resulting local strains in the lamellar microstructure are computed.

9:40 AM

MICROSTRUCTURAL EFFECTS ON THE CREEP, LOW CYCLE FATIGUE AND CRACK PROPAGATION BEHAVIORS OF Ti-47Al-2W-0.5Si: *Valentino Lupinc*[1]; Massimo Marchionni[1]; Mohamed Nazmy[2]; Giovanni Onofrio[1]; Mark Staubli[2]; [1]CNR-TEMPE, Via Cozzi 53, Milan 20125 Italy; [2]ABB Power Generation, KWTM.D, Baden, CH-5401 Switzerland

In the present investigation, the effect of microstructure on the tensile, creep, low cycle fatigue and fatigue crack properties is studied in the cast and HIP'ed Ti~47Al-2W-0.5Si alloy. Two heat treatment schedules were applied to produce two different types of microstructures, i.e. the duplex (globular gamma and lamellar alfa2/gamma) and the nearly lamellar types. The tensile strength and creep behaviour of this alloy, in the temperature range of 700-850ϒC, have been determined and correlated to the corresponding microstructures. In addition, the low cycle fatigue and fatigue crack propagation behaviours in this alloy have been studied at different temperatures. The results on the creep behaviour showed that the alloy with lamellar microstructure has an improved creep strength as compared with that of the duplex microstructure. The static and dynamic mechanical properties of this alloy were also compared with those of nickel base superalloys.

10:00 AM

K5 WROUGHT TiAl ALLOYS: DESIGN, PROCESSING, AND PROPERTIES: *Young-Won (Y-W.) Kim*[1]; [1]UES, 4401 Dayton-Xenia Rd., Dayton, OH 45431 USA

Significant improvements in tensile properties in wrought gamma TiAl K5 alloys have been made through controlling lamellar grain-size (GS) and spacing (LS) and grain-boundary (GB) morphology. GS refinement has been achieved by several methods, including: small boron additions, novel processing routes, two-phase-field heat treatments, and the combinations. LS was varied by controlling cooling-rate and scheme which are often chemistry- or processing-specific. The microstructural refinements were found to also enhance creep-resistance, fatigue-strength and damage-tolerance at temperatures below BDTT; however, at a certain expense of higher-temperature deformation/fracture resistance. LS refinement tends to reduce GB serration thereby lowering RT ductility and fracture resistance. Recently, progresses have been made in reducing the refinement-induced deficiencies through chemistry modification and/or microalloying and process/heat-treatment control. This progress report: 1) discusses designing K5 alloys based on the experimental findings and fundamental knowledge; 2) evaluates K5-series alloys with specific property data set; and 3) assesses the issues for further improvements.

10:30 AM INVITED PAPER

EFFECTS OF MINOR ALLOYING ADDITIONS ON MIROSTRUCTURES AND MECHANICAL PROPERTIES OF LAMELLAR TiAl ALLOYS: *C. T. Liu*[1]; P. J. Maziasz[1]; D. J. Larson[1]; [1]Oak Ridge National Laboratory, Metals and Ceramics Division, P.O. Box 2008, Oak Ridge, TN 37831-6115 USA

This paper provides a comprehensive review of our recent work on the effects of minor alloying additions on lamellar structures and mechanical properties of dual-phase TiAl alloys. The base alloy Ti-47Al-2Cr-2Nb (at. %) was alloyed with equal and less 1% of B, W, Mo, and/or Ta, and all the alloys were prepared by powder and ingot metallurgy. The microstructural features were controlled by hot-extrusion temperature, and mechanical properties were evaluated by tensile testing at temperatures to 1000ϒC. Microstructural features, including colony size, interlamellar spacing, interfacial segregation and particle composition, were characterized by optical microscopy, electron microprobe analyses, transmission electron microscopy, and atom probe field ion analyses. The Hall-Petch equations are found to be applicable to both the yield strength and tensile ductility at room and elevated temperatures. Colony size is a major parameter controlling the tensile ductility, and the yield strength is solely controlled by interlamellar spacing. The strengthening effect of minor alloying additions essentially comes from their refinement of lamellar spacing, rather than from a classic solute hardening effect.

11:00 AM

THE EFFECT OF COMPOSITION ON THE STABILITY AT 700°C AND ON THE MECHANICAL PROPERTIES OF GAMMA TITANIUM ALUMINIDES: *Richard Raymond Botten*[1]; Alastair Bryan Godfrey[1]; Michael H. Loretto[1]; [1]University of Birmingham, IRC in Materials for High Performance Applications, Edgbaston, Birmingham, West Midlands B15 2TT UK

Recent research has shown that the fully lamellar microstructure is not thermally stable at its predicted use temperature (700ϒC). Decomposition of the alpha-2 laths occurs, along with the formation of precipitates rich in alloying elements. The current research concentrates on two alloys one based on the Ti-47at.%Al system with low alloying additions, 1-2at.% of each individual alloying element, and on the Ti-44at.%Al system with higher alloying additions, 4-8at.% of each individual alloying element. Both alloys have been heat treated to produce the fully lamellar microstructure and then, exposed in air at 700ϒC for 3000h. Microstructural changes have been investigated using scanning and transmission electron microscopy. Mechanical properties have been assessed in terms of room temperature tensile properties and creep rates at 700ϒC under a stress of 200MPa.

11:20 AM

CREEP OF GAMMA TITANIUM ALUMINIDES: ENGINEERING OBSERVATIONS AND REQUIREMENTS FOR COMPONENTS: *Ian J. Perrin*[1]; [1]Mechanical Engineering Centre, GEC ALSTHOM, Cambridge Rd., Whetstone, Keicester Le8 6LH UK

Alloys based on the gamma titanium aluminide intermetallic compound have a combination of properties which offer many benefits for low pressure turbine blades of industrial gas turbines. These benefits are discussed and it is identified that creep strength is particularly important for such components which are required to operate at high loads for long periods of time. These creep strength requirements are assessed using simple models. This enables absolute strength requirements to be defined and identifies the most crucial aspects of the creep response. This information should help to guide future alloy development. In addition, the creep response of gamma-TiAl alloys is reviewed from an engineering perspective. Features discussed include basic behaviour (under both uniaxial and multiaxial states of stress), creep models and life assessment methods. The various concepts and methods are illustrated with typical data for a gamma-TiAl alloy.

11:40 AM

IMPROVEMENT OF METALLURGICAL PROCESSING PARAMETERS FOR EPM TiAl-1.4Mn-2Mo ALLOY: J. K. Kim[1]; *Sun-Keun*

Hwang[1]; S. W. Nam[2]; N. J. Kim[3]; [1]Inha University, Metall. Eng., 253 Yonghyeon-Dong, Nam-Gu, Incheon 402-751 Korea; [2]KAIST, 373-1 GuSeong-Dong, Daejeon, ChungNam 305-701 Korea; [3]POSTECH, Mt. 31, HyoJa-Dong, Pohang, GyungBug 709-784 Korea

Laboratory alloy TiAl-1.4Mn-2Mo was synthesized by elemental powder Metallurgy (EPM) and the tensile properties and the creep resistance were evaluated. The mechanical properties were comparable to or better than other gamma alloys made by ingot metallurgy. In the EPM processing of the laboratory alloy, it was important to select a fine Mo powder and to conduct a proper pre-hot extrusion treatment in order to ensure minimal porosity and uniform microstructure. Controlling the Mo powder size was necessary because of concerns on Kirkendall porosity and ¥â-phase formation. Pre-hot extrusion treatment was required to stabilize intermediate phases such as Ti2MoAl and TiAl3. Various post-extrusion heat treatments were devised to refine the final lamellar microstructure to a range of 30§≤ in packet size. Overall the present work supports the viability of the PM approach in developing gamma alloys.

12:00 PM

PROPERTIES OF FORGED GAMMA-TiAl COMPRESSOR BLADES: *Thomas Haubold*[1]; *Dan Fagaraseanu*[1]; [1]BMW Rolls-Royce GmbH, Mats. Tech., Hohemarkstr. 60-70, Oberursel, Hessen 61440 Germany

TiAl compressor blades and vanes in aeroengines would offer a potential for weight saving and increased work temperature above superalloys commonly used for this application (Inco718). Extrusion and isothermal forging has been investigated as processing routes for manufacturing. The blade life depend mainly on material fatigue behaviour, the static and dynamic stress fields in the blade, the load history and environment. Hence main properties for component design such as fatigue behaviour (HCF/LCF), crack growth, tensile and creep properties have been tested for different processing routes for temperatures up to 700ϒC. The fracture surface and microstructure were characterised by light and scanning electron microscope analysis. Component vibrations test are planned to prove the blade resonant mode behaviour and correlate the results with material test data. This research has been supported by BMBF (MaTech) 03N 3025

TUESDAY AM

LEACHING THEORY PROCESS DEVELOPMENT & INDUSTRIAL PRACTICE: Copper Leaching

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

Program Organizers: Akram Alfantazi, Falconbridge, Ltd., Falconbridge Technology Centre, Falconbridge, Ontario P0M 1S0 Canada; Arash Kasaaian, Elkem Metals Company, Marietta, OH 45750 USA; Alexandre J. Monteiro, Indosuez Capital Emerging Markets, Sao Paulo, SP 01311-902 Brazil

Tuesday AM Room: 1B
March 2, 1999 Location: Convention Center

Session Chairs: Dr. A. Alfantazi, Falconbridge, Ltd Falconbridge Technology Centre, Falconbridge, Ontario P0M 1S0 Canada.; Dr. G. Demopoulos, McGill University

8:30 AM

AMMONIA LEACHING OF COPPER CONCENTRATES - COMMERCIAL APPLICATION: *Nathaniel Arbiter*[1]; [1]Nathaniel Arbiter Associates, Inc., 6300 S. Upper Valley Rd., Vail, AZ 85641 USA

First commercial plants for ammonia leaching (Alaska-copper carbonate ores; Michigan-native copper tailings) were followed later by development of flowsheets for sulphide concentrate leaching. Two of these resulted in full scale plants. 1) Annconda's Arbor Plant started up in 1974 with a design capacity of 35,000 tons/year of cathodes, produce by ammonia leaching (AL) with oxygen, followed by solvent extraction (SX) and electrowinning (EW). This shut down in 1977 after experiencing operating problems due to sulphate disposal as gypsum. 2) BHP's Coloso plant in Chile leached part of Eacondida's concentrates, using AL/SX/EW but with $O_{2/}$ from air to avoid mulphate production. Starting up in late 1994, it shut down in mid-1998, after failing to reach design capacity and experiencing problems with its technology. This paper will review the flowsheets, suggesting changes to improve metallurgy. Disposal of ammonium sulphate produced by sulphide oxidation was and is critical. Alternatives are to find markers for it; or to use line for precipitating $CaSo_4$, and recovering ammonia, other alternatives will also be discussed.

8:50 AM

COMPUTATION OF AQUEOUS SPECIES AND ACTIVITIES AND SOLUTION EQUILIBRIA IN HEAP LEACHING OF A LOW-GRADE SULPHURIC COPPER ORES: *Tero Kolhinen*[1]; Heikki Jalkanen[1]; [1]Helsinki University of Technology, Laboratory of Metallurgy, Vuorimiehentie 2, Espoo, P.O. Box 6200, Espoo FIN-02015 Finland

The aim of the study was to establish a thermodynamically consistent route for heap leaching of sulphide ore of copper using ferric iron as a leaching agent. The computer program, CHEMSAGE, was used for predicting the equilibrium behaviour of the leach solution. Pitzer's model was included to account for the expected non-ideal model. This model is a virial coefficient expansion of the Debye-Hückel equation and is considered suitable for the high ionic strengths chracterestic of heap solutions. The leach solution was modelled using heat capacity functions for aqueous species. Pitzer model parameters were taken from the literature or estimated from solubility data for sulphates. Gradual dissolution of copper sulphide minerals and precipitation ranges for metal sulphates have been calculated within a temperature region of 0 to 75°C. These results have been used to provide a basis for investigating the thermodynamic stability of various routes for the heap leaching process.

9:10 AM

RESULTS OF LABORATORY AND PILOT TESTWORK: LEACHING AND PROCESSING OF COMPLEX CONCENTRATES CONTAINING ZINC, LEAD AND COPPER: *L. Filip*[1]; T. Velsa[2]; A. Mezei[3]; [1]Ceronef S.A. Buin, Maro Romania; [2]IAMN S.A., Bucarest, Romania; [3]Lakefield Research, Ltd., Canada

The roast leach electra-recovery process for zinc was modified to treat two typical complex concentrates containing zinc, lead, copper, gold and silver. Laboratory testwork results indicated that the optimum roasting temperature ranged from 700 to 800ϒC in order to produce acceptable residual sulphur levels. The calcined concentrate was subjected to a three stage lench sequence. The resulting leach solution was purified by hernattic precipitation and directed in the recovery of copper and zinc by solvent extraction and electrolysis. The lead and precious metals were recovered by alkaline smelting and subsequent electrolytic purification. A flowsheet was produced based on the laboratory testwork results, and verified in a large scale pilot plant. The recoveries produced during the pilot plant operation ranged from 90 to 92% for zinc and copper, 85% for lead and 90% for gold and silver, respectively.

9:30 AM

ATOMIC FORCE SPECTROSOPIC AND ELECTROCHEMICAL IMPEDANCE SPECTROSCOPIC CHARACTERIZATION OF SULFUR LAYER DURING ACIDIC LEACHING OF CHALCOPYRITE: *M. Misra*[1]; K. Narayanan[1]; B. K. Jena[1]; [1]University of Nevada, Dept. of Chem. & Metall. Eng./MS 170, Reno, NV 89557 USA

The utilization of Atomic Force Microcopy (AFM) along with Electrochemical impedance Spectroscopy (EIS) is a new approach in the characterization of the sulfur layer formed during chalcopyrite leaching. The AFM imaging was performed in conjunction with EIS to analyze sulfur growth, grain size, roughness and peak height. In addition the critical resistance of the sulfur layer and rate law for sulfur layer formation were calculated.

9:50 AM

FEASIBILITY OF SELECTIVE EXTRACTION OF NICKEL AND COPPER FROM COMPLEX SULPHIDE ORE BY PRESSURE LEACHING: *J. X. Guo*[1]; [1]Queen's University, Kingston, Ontario K7L 3N Canada

The typical feed to pressure leach process, as practiced today in nickel sulfide industry, is intermediate nickel-bearing materials such as anode nickel, nickel-copper mattes, or at least nickel sulfide concentrates. Flotation continues to be an indispensable step without which the mining and the subsequent metallurgy of low-grade and complex ore bodies would be prohibitively expensive, However, it has been gradually recognized that the importance of flotation may decline as other methods such as hydro and pyrometallurigal processes may be better qualified to treat refractory ores in which the useful mineral is very finely disseminated and adequate liberation from the gangue is not possible. This paper summarizes the laboratory study in applying pressure leach process to the selective extraction of copper and nickel directly from a complex sulfide ore which mainly consists of chalcopyrite, pentlandite and pyrrhotite. The results indicate significant differences in the relative metal-releasing rates between different minerals by controlling process variables. Nickel-bearing sulfide metals decompose more readily than chalcopyrite while most of iron sulfides remain in the residue in the form of hermatite. Temperature was found to exhibit the strongest impact on selectivity, while a reduced oxygen concentration in combination with a suitable between retention time also yielded very effective selective extraction rates. A two stage pressure leach process was desired and tested at laboratory scale resulting in satisfactory selectivity and overall recovery.

10:10 AM

OPTIMISATION OF THE LEACH CONDITIONS FOR A COPPER/URANIUM ORE: *R. J. Ring*[1]; D. E. Collier[1]; L. Tan[1]; A. Day[1]; S. J. Macnaughton[1]; [1]Australian Nuclear Science and Technology Organization, Environment Division, PMB 1, Menai, NSW 2234 Australia

The Olympic Dam deposit in South Australia contains 24 copper and 0.06% uranium, which are present as bornite, chalcopyrite, uraninite, brannerite and coffinite. The copper is principally recovered using flotation. The floatation tailings, which contain the bulk of the uranium, and typically 0.3% copper, are leached using sulfuric acid and ax oxidant at ambient pressure. This paper describes the results from a detailed investigation of the leaching behaviour of this ore. The influence of acid strength, ferric ion concentration, redox potential and temperature on the dissolution of uranium, copper and gangue minerals was studied. Experimental data was obtained from SEM analysis of individual mineral grains, extensive mineralogical studies and batch leach tests. The maximum extractions of copper and uranium determined experimentally were in good agreement with those predicted from SEM determination of the proportions of refractory chalcopyrite and brannerite in the ore. The leaching rate of copper was found to be independent of acidity over the range 20 g L-1 to pH 2.0, but was strongly dependent on temperature and ferric ion concentration. Uranium extraction showed a weak dependence on acidity, Arrhenius temperature dependence and a complex co-dependence on ferric ion concentration and redox potential. A kinetic model has been developed that predicts copper and uranium dissolution and also accounts for gangue dissolution. This model is being incorporated into a more comprehensive model that can be used to predict leach performance and reagent consumption for specific ore samples.

10:30 AM

FLUOROCHEMICAL SURFACTANT USE IN HEAP LEACHING: THEORY AND PRACTICE: *Michael J. Sierakowski*[1]; [1]3M Performance Chemicals & Fluids Laboratory, 3M Bldg. 236-2A-01, St. Paul, MN 55144 USA

Surfactants play a vital role in the mining industry and flurochemical surfactants, in particular, have demonstrated utility in several hydrometallurgical operations including their use leach operations. Surfactant aided wetting to increase lixiviant contact with one can result in accelerated leach kinatics and increased metal recovery. The critical aspects of establishing fluorochemical surfactant utility by determining their mode of best use, determining amenable ore types, the development of column testing procedures to overcome sample variability, and the nuances of large-scale field testing followed by partnering efforts with mining operations to gain industry acceptance illustrate the commitment required to bring a product from concept to commercial use in this industry.

LIGHT WEIGHT ALLOYS FOR AEROSPACE APPLICATIONS V: Ultra Light Weight Materials

Sponsored by: Structural Materials Division, Non-Ferrous Metals Committee

Program Organizers: Eui W. Lee, Naval Air Warfare Center, Code 4342, MS5, Patuxent River, MD 20670 USA; William Frazier, Naval Air Warfare Center, Aircraft Div., Patuxent River, MD 20670-1908 USA; K. Jata, Wright-Patterson Air Force Base, WL-MLS, Dayton, OH 45433-7718 USA; Nack J. Kim, Center for Adv. Aerospace Materials, Pohang 790-330 Korea

Tuesday AM Room: 9
March 2, 1999 Location: Convention Center

Session Chair: K S Shin, Seoul National University, Dept. of Mats. Sci. and Eng., Kwanak-ku, Seoul Korea

8:30 AM

ELEVATED TEMPERATURE DEFORMATION OF NANO-SCALE DISPERSION STRENGTHENED ALUMINIUM ALLOYS: *Emma Jane Minay*[1]; Richard J. Dashwood[1]; Henry McShane[1]; [1]Imperial College, Mats. Process. Group, RSM, Prince Consort Rd., South Kensington, London SW7 2BP UK

Nano-scale reinforced aluminium alloys are being developed for applications at 523-573K as a lighter alternative to titanium based materials in the aerospace industry. Results of an investigation of the deformation behaviour of dispersion strengthened aluminium based materials produced by mechanically alloying aluminium and aluminium 0.35wt% lithium 1wt% magnesium powders with 13nm diameter Al_2O_3 powder and 23nm diameter TiO_2 powders are reported. Constant strain rate compression tests were performed at temperatures of 523, 623, 723 and 823 K and strain rates of $5x10^{-5}$ to $10^{-1}s^{-1}$. The effect of volume fraction of dispersoid, type of dispersoid and solute additions on the deformation behaviour is reported. The materials were found to work soften and undergo compressive failure. The deformation behaviour is extremely sensitive to temperature and insensitive to strain rate and is shown to be associated with a threshold stress resulting from a particle dislocation interaction. The strain rate-stress relationship has been compared to the detachment model of Rosler and Arzt. By introducing a variable value for the detachment stress it is possible to reflect the correct temperature dependance of the stress-strain rate relationship.

8:55 AM

THE JOMINY END QUENCH FOR LIGHT WEIGHT ALLOY DEVELOPMENT: *Joseph William Newkirk*[1]; [1]University of Missouri-Rolla, Dept. of Metall. Eng, Rolla, MI 65409 USA

The Jominy end quench test is well known as a method of measuring hardenability in steels. In light weight alloys there is a desire to determine the effect of quenching on final properties after heat treating. The Jominy end quench test offers a method for studying many quenching conditions with a minimum of samples. The potential of the Jominy End Quench and a modified end quenching apparatus for developing new understanding of the complex response of light weight alloys to processing conditions, especially quenching, will be presented. In addition, several examples will be illustrated.

9:20 AM

PROCESSING AND CHARACTERIZATION OF Be-Al ALLOYS: *Xiao-Dong Zhang*[1]; Jorg Wiezorek[1]; Fritz Grensing[2]; Glyn Meyrick[1]; Harry Lipsitt[1]; Hamish Fraser[1]; [1]The Ohio State University, Dept. Mats. Sci. Eng., 2041 College Rd., Columbus, OH 43210 USA; [2]Brush Wellman, 14710 West Portage River South Rd, Elmore, OH 43416 USA

Be-Al alloys, due to their high elastic modulus, low density and a relatively high melting point, are one of the most promising light weight materials for aerospace and high speed ground transport applications. It has been reported recently that Be-Al alloys can be cast and extruded successfully, and exhibit reasonably promising mechanical properties. However there is lack of fundamental understanding of the physical metallurgy of these alloys, such as the formation of the cast microstructure which has previously been attributed to the existence of a submerged metastable monotectic reaction in high Be-Al compositions. In the present study we will present and discuss the results on the microstructural characterization on both as-cast and extruded alloys using SEM and TEM. The fracture and deformation mechanisms observed from tensile and compressive test samples will also be presented and discussed in terms of the mobility and the nature of dislocations in Al and Be phase respectively. More recent work on the alloy development will also be presented. This work has been supported by a grant from the Office of Naval Research with Dr. Steven J. Fishman as program manager.

9:45 AM

STRENGTHENING EFFECTS OF Al AND Mn ON WROUGHT Mg-6WT%Zn ALLOYS: *S. C. Park*[1]; K S Shin[1]; [1]Seoul National University, School of Mats. Sci. and Eng., Shinrimdong, Center for Advanced Aerospace Mats., Seoul 151-742 Korea

In order to evaluate the effects of Al and Mn additions on the strengthening of the extruded Mg-6wt%Zn alloys, the age hardening response and tensile properties were examined with different amounts of alloying elements and heat treatments. The microstructures of the aged specimens were examined by STEM. After the double aging treatment the peak hardness was found to increase after shorter aging time. The optimum tensile properties were obtained with the addition of 1 wt% Mn. The addition of 2 wt. % Al to the Mg-6 wt % Zn alloy increased UTS with a small increase in YS. in the double aging condition. The tensile elongation was found to increase remarkably with the Al addition after solution heat treatment and double aging treatment. The effects of Al and Mn addition will be discussed in the light of the experimental results.

10:10 AM

THE MECHANICAL PERFORMANCE OF METAL MATRIX COMPOSITE JOINTS: *Damon D. Brink*[1]; S. A. Waltner[1]; C. G. Levi[1]; F. A. Leckie[1];[1]University of CA at Santa Barbara, Mats., Santa Barbara, CA 93106 USA

The mechanical performance of joints in MMCs will be discussed with regard to the interplay between metal-ceramic interfaces, metal constraint and the geometry of composite -monolith transitions. Model joints consisting of aluminum matrix composite subelements separated by a thin metal interlayer were fabricated by pressure infiltration of an Al-4.5% Mg alloy into preforms of polycrystalline alumina fibers containing planar discontinuities, thus minimizing processing defects and ensuring interface integrity. The high degree of constraint and concurrent build up of large hydostatic stresses in the metal layer allows simple butt joints to support applied loads in excess of 3 times the metal yield strength. The composite /interflayer interface fails at these stress levels due to the coalescence of debonded regions at the fiber ends. Increasing metals constraint to the order of the fiber diameter achieved by reinforcing the interlayer with particles inhibits this mode of failure and results in strength increases of up to 50%. The failure mechanisms operating in these joints will be discussed in terms of the relevant length scales of plasticity associated with differences in interfacial microstructure. Changes in the evolution of the interlayer stress state associated with various levels of constraint will also be considered.

10:35 AM

DEVELOPMENT OF STEEL FOAM AS A LIGHT WEIGHT MATERIAL FOR AEROSPACE APPLICATIONS: *Mike Yu*[1]; Harald Eifert[1]; Markus Knuwer[2]; Markus Weber[2]; [1]Fraunhofer Resource Center, Mats., Newark, DE USA; [2]Fraunhofer Institute for Applied Materials Research, Bremen Germany

A new powder metallurgy process for the production of metallic foams was developed for a range of alloys including Al and steel. This method allows for a direct net-shape fabrication of foamed parts with relatively homogeneous and isotropic pore structure. Metallic foam made by this approach has a high volume fraction of porosity and exhibits a closed-cell microstructure. This type of microstructure is particularly attractive for applications requiring high specific stiffness and energy absorption. This paper will report the result of a project sponsored by the ONR in developing steel foam for lightweight structure. To date, the obtained foam steel has a range of density from 3-5 gm/cm3. The advantage in weight reduction in steel may enable its use for aerospace applications.

11:00 AM

DEFORMATION BEHAVIOUR OF 7075Al/SiCp COMPOSITE DURING MULTI-PASS DEFORMATION AT HIGH TEMPERATURES: A. Razaghia[1]; D. Yu[1]; H. Asanuma[2]; T. Chandra[1]; [1]Department of Materials Engineering, Wollongong University, Wollongong, NSW, 2522, Australia; [2]Chiba University, Department of Mechanical Engineering; Chiba City, 263, Japan

Hot Deformation behavior of 7075 aluminium alloy containing 15 vol% of SiC particles (average size of 14 μm) and the monolithic alloy was studied at 300 and 400°C at constant strain rate of $1s^{-1}$ under condition of uniaxial compression. The effect of delay between two consecutive passes on the high temperature mechanical strength and microstructural development was examined. The results showed that the fractional softening (%FS) increased in both reinforced and monolithic alloys when the deformation temperature increased from 300 to 400°C, but monolithic alloy showed a slightly higher FS compared to composite under identical deformation conditions. TEM examination revealed that the monolithic alloy and composite contained almost similar substructures after either single or double pass deformation at a given temperature irrespective of interpass hold time. However, some subgrain growth was observed in these materials during holding after deformation at 400°C, but this was not the case at 300°C. The absence of subgrain growth at lower temperature can be attributed to pinning effect by fine dispersions present in the matrix. The structural study also showed that static recrystallization did not occur in these materials during hold time between passes, and the fractional softening occurs mainly due to static recovery.

11:25 AM

CORROSION FATIGUE BEHAVIOR OF THE HIGH-STRENGTH MAGNESIUM ALLOY AZ 80: M. Hilpert[1]; L. Wagner[1]; [1]Technical University of Brandenburg at Cottbus, P.O. Box 10 33 44, 03013 Cottbus, Germany

The high-strength magnesium alloy AZ 80 was received as extruded bar. Specimens were machined with the load axis parallel to the extrusion (L) direction as well as parallel to the radial (R) direction. Axial fatigue tests were performed on electrolytically polished hourglass shaped specimens in fully reversed loading (R=-1) using a resonance testing machine at frequencies of roughly 100 Hz. Tests were performed in an aequious 3.5% NaCl solution and in lab air. In addition, some tests were conducted in vacuum. To improve the fatigue performance, mechanical surface treatments were applied. Results on shot peened and roller-burnished specimens will be compared with the electrolytically polished reference. Fatigue performance of the various conditions will be interpreted in terms of crystallographic texture, surface roughness, work hardening and residual compressive stresses.

MATERIALS PROCESSING FUNDAMENTALS: Thermodynamics and Kinetics

Sponsored by: Extraction & Processing Division, Process Fundamentals Committee; Jt.Extraction & Processing Division/Materials Processing and Manufacturing Division, Synthesis, Control and Analysis in Materials Processing Committee

Program Organizers: W.D. Cho, University of Utah, Dept. of Metall. Eng., Salt Lake City, UT 84112 USA; Huimin Liu, UES, Inc., Annapolis, MD 21401 USA; Srinath Viswanathan, Oak Ridge National Lab, P.O. Box 2008, Bldg. 4508, Oak Ridge, TN 37831-6083 USA

Tuesday AM Room: 5A
March 2, 1999 Location: Convention Center

Session Chairs: Weol D. Cho, University of Utah, Dept. of Metall. Eng., Salt Lake City, UT 84112 USA; J. B. Hisky, University of Arizona, Dept. of Mats. Sci. and Eng., Tuscon, AZ 85721 USA

8:30 AM

THERMODYNAMIC STUDY OF ZINC-IRON INTERMETALLICS BY MASS SPECTROMETRY: Kazuaki Mita[1]; *Masafumi Maeda*[1]; [1]University of Tokyo, IIS, 7-22-1 Roppongi, Minato, Tokyo Japan

There are various intermetallic compounds in Zn-Fe system. We synthesized those at about 500ϒC. Specimen was examined chemically and Xray diffraction was applied to ensure the formation of intermetallics compounds. Material containing two phases was placed in a knudesen type effusion cell and mass spectrum studied to evaluate the vapor pressure of Zinc. Thermodynamics of intermetallics are then evaluated through measured intensity.

8:55 AM

SIMULTANEOUS SULFATION OF CALCIUM OXIDE AND MAGNESIUM OXIDE IN CALCINED CMA (CALCIUM MAGNESIUM ACETATE): *Dong Hoon Han*[1]; Hong Yong Sohn[1]; [1]University of Utah, Dept. of Metall. Eng., Salt Lake City, UT 84112 USA

The kinetics of the simultaneous sulfation by sulfur dioxide and oxygen of CaO and MgO in calcined CMA (calcium magnesium acetate) were investigated experimentally and compared with a rate equation obtained based on the kinetics of each reaction. The experiments were carried out in the temperature range from 700 to 830ϒC and under the S0[2] concentrations of 0.3 to 1 mol%. The oxygen concentration and the particle size were 5% and-325+400 mesh (37-44um), respectively Each sample was calcined completely by heating it at about 10ϒC /min up to 1000ϒC under a nitrogen atmosphere, before the temperature was lowered to the sulfation temperature. According to the ranges of partial pressure of sulfur dioxide and temperature, there exist three regions for the sulfation reaction: region I in which neither oxide is sulfated, region II in which only CaO is sulfated, and region III in which both oxides are sulfated. To investigate separate sulfation kinetics of each solid in calcined CMA, the sulfation kinetics of the CaO content were obtained in region II. The MgO sulfation kinetics were obtained in region III after the CaO content was fully sulfated to CaSO4. The experimental results were in good agreement with the theoretical predictions according to the combined simultaneous rate equation.

9:20 AM

REDUCTION OF CALCIUM SULFATE BY HYDROGEN TO PRODUCE CALCIUM SULFIDE AS A REDUCTANT OF SULFUR DIOXIDE TO ELEMENTAL SULFUR: *Byung-Su Kim*[1]; Hong Yong Sohn[1]; [1]University of Utah, Dept. of Metall. Eng., Salt Lake City, UT 84112-0114 USA

The reaction between calcium sulfate and hydrogen is of interest both as a means of regenerating calcium sulfide as a reductant of sulfur dioxide to elemental sulfur and for producing elemental sulfur from gypsum. The kinetics of this reaction were measured using a thermogravimetric analysis technique in the absence and presence of nickel catalyst, and the reactivity of regenerated calcium sulfate investigated. The reaction temperature was varied between 973 and 1153K, while hydrogen partial pressures of 2~ 86 kPa were utilized. At 1073K in the hydrogen partial pressure of 86 kpa, 60% of the original calcium sulfate in the absence, and 95% in the presence, of the nickel catalyst was converted to calcium sulfide in one hour. A nucleation and growth model was found to fit the reaction rate reasonably well. The reactivity of the regenerated calcium sulfate, with or without the catalyst, remained similar to that of the original sample even after three cycles.

9:45 AM

PSEUDO-BINARY PHASE DIAGRAM OF THE CUSPIDINE - CAF2 SYSTEM - RELATING TO MOLD FLUX FOR CONTINUOUS CASTING OF STEEL: *Hiroyuki Fukuyama*[1]; Takashi Watanabe[1]; Masahiro Susa[2]; Kazuhiro Nagata[1]; [1]Tokyo Institute of Technology, Dept. of Chem. and Mats. Sci., 2-12-1 Ookayama, Meguro-ku, Tokyo 152-8552 Japan; [2]Tokyo Institute of Technology, Dept. of Metall. Eng., 2-12-1 Ookayama, Meguro-ku, Tokyo 152-8552 Japan

Recently, the role of cuspidine, $3CaO2SiO_2CaF_2$, has been of considerable practical concern in mold flux for the continuous casting process of steel. Cuspidine crystallizes in almost all kinds of flux films during the casting of steel and it affects the thermal properties of the flux. Therefore, the crystallization causes a non-uniform heat flux between the strand and the mold, which may lead to the surface defects of slab due to the thermal stress. However, very little work is currently available in the published literature on the fundamental physicochemical properties of cuspidine, such as the phase diagram, the free energy of the formation and the thermal conductivity, etc. In the present paper, one of the most important data to design mold powder, i.e. the phase diagram of the system cuspidine - CaF_2 has been studied by electron probe X-ray microanalysis (EPMA) and X-ray diffractometry (XRD).

10:10 AM BREAK

10:20 AM

KINETICS OF DEHYDRATION OF $FeSO_4$-$7H_2O$ UNDER DIFFERENT ATMOSPHERES: *N. Kanari*[1]; I. Gaballah[1]; C. Mathieu[2]; N. Neveux[2]; O. Evrard[2]; [1]LEM, Associated to CNRS UMR 7569, Mineral Process. and Environmental Eng. Team, ENSG, INPL, Vandceurve BP 40, 54501 France; [2]Universite Henri Poincare Nancy I, Laboratoire de Chimie du Solide Minerale, Vandceuvre Bp 239, 54506 France

Hydrated ferrous sulfate is a by-product of titanium and surface treatment industries. The majority of this product has to be waste disposed that is considered as a supplementary cost for these industries. Recently, the ferrous sulfate partially dehydrated was successfully used for the synthesis of a new superoxidant material containing iron in hexavalent state (Fe^{VI}). The kinetics of dehydration of FeSO4~7H2O under neutral, oxidizing and chlorinating atmospheres were studied by thermogravimetric and differential scanning calorimetry analysis. The obtained products were analyzed by X-ray diffraction and Mossbauer spectroscopy. The effects of temperature, gas velocity, type of sulfate, etc. on the dehydration rate were defined.

10:45 AM

KINETICS OF OXYCHLORINATION OF MAGNESIUM OXIDE: *N. Kanari*[1]; E. Allain[2]; I. Gaballah[1]; [1]LEM, CNRS UMR, Mineral Process. and Environmental Eng. Team, ENSG, INPL, Vandceure BP 40, 54501 France; [2]University of Missouri-Rolla, School of Mines and Metallurgy, Center for Pyrometallurgy, 215 Fulton Hall, Rolla, MO 65401 USA

Kinetics of oxychlorination of MgO by Cl_2+$0_2$2 were in the temperature range of 850ϒC to 1025°C using thermogravimetric analysis. The effects of $C1_2/0_2$ ratio, gas velocity, temperature and partial pressure of reactive gases reaction rate were investigated. The apparent activation energy of MgO oxychlorination was about 214 kJ/mol. The reaction orders with respect to Cl_2+0_2, Cl_2 and 0_2 at 950ϒC were about 0.65, 0.98, and -0.37, respectively. Some data concerning the oxychlorination of MgO were compared with those of Cr_20_3 and $MgCr_2O_4$ contained in

chromite mineral. Efficiency of using oxychlorination for the removal of iron oxides contained in magnesia was demonstrated.

11:10 AM
KINETIC STUDY ON THE LIME ENHANCED REDUCTION OF CHALCOCITE WITH CARBON: *M. C. Ruiz*[1]; R. Padilla[1]; [1]University of Concepcion, Dept. of Metall. Eng., Edmundo Larenas, Concepcion 270 Chile

The conventional pyrometallurgical methods to treat copper sulfide concentrates include generally one or more oxidizing steps where the formation of $S0_2$ gas can not be prevented from the economical point of view and the nature of some of the processes in which SO_2 is produced, its complete capture is not feasible; therefore, an important fraction is released to the atmosphere as fugitive emissions. In this research, the reduction of chalcocite was studied in the presence of lime as an alternative method which overcomes the pollution problems related to SO_2 emissions. The effects of temperature, time, concentration of the reactants carbon and CaO on the reductions rate were studied. From these variables, temperature affects most the reduction rate. Conversions over 95% can be obtained in less than 20 um at temperatures over 1000ϒC. The measured partial pressures of the gaseous components indicated that the chalcocite reduction proceeds through the gaseous intermediate species CO, $C0_2$, and that the overall kinetics was controlled by the Boudouard reaction. The kinetic model ln(1 -X)= kt fits well the experimental data, and an apparent activation energy of 314 kJ/mol was calculated for the temperature range 800ϒC-1050ϒC.

11:35 AM
KINETICS OF SCORODITE FORMATION: *Preeti Pande*[1]; J. B. Hiskey[1]; [1]University of Arizona, Dept. of Mats. Sci. and Eng., AZ USA

The kinetics of high-pressure, hydrothermal crystallization of the arsenic containing mineral, scorodite is investigated. An amorphous FeAsO4 particulate is formed in solution, and its transformation into the As-stabilized, crystalline scorodite phase is followed both by a selective dissolution method and by XRD. The effects of treatment temperature and of the iron and arsenic concentrations on the kinetics of the transformation are discussed.

MICROMECHANICS AND MICROMECHANISMS OF DEFORMATION AND FRACTURE: A SYMPOSIUM IN HONOR OF PROFESSOR ALI S. ARGON: Session III

Sponsored by: Structural Materials Division, Mechanical Metallurgy Committee, High Temperature Alloys Committee
Program Organizers: K. Jimmy Hsia, University of Illinois, Dept. of Theoretical & Appl. Mech.,Urbana, IL 61801 USA; Mary Boyce, Massachusetts Institute of Technology, Dept. of Mech. Eng., Cambridge, MA 02139 USA; Tresa M. Pollock, Carnegie Mellon University, Dept. of Metall. Eng. & Mat. Sci., Pittsburgh, PA 15213 USA

Tuesday AM Room: 14B
March 2, 1999 Location: Convention Center

Session Chairs: Tresa M Pollock, Carnegie Mellon University, Dept. of Mats. Sci and Eng., Pittsburgh, PA 15213 USA; Hael Mughrabi, University Erlangen-Nuernberg, Erlangen, Bavaria D-91085 Germany

8:30 AM INVITED PAPER
LONG-RANGE INTERNAL STRESSES: THE COMPOSITE MODEL AND ITS CONSEQUENCES: *Hael Mughrabi*[1]; [1]University Erlangen-Nuernberg, Werkstoffwissenschaften, Martensstr 5, Erlangen, Bavaria D-91058 F.R. Germany

The original discussion about the role of long-range internal stresses in strain-hardened (single-phase) metals was based on dislocation pile-ups as the classical sources of long-range internal stresses. The problems encountered were related to the fact that, while there was abundant evidence in favor of deformation-induced long-range internal stresses, dislocation pile-ups were rarely observed. This problem was resolved theoretically by the introduction of the composite model of heterogeneous dislocation distributions which could also be verified experimentally. The main idea of the composite model is that any heterogeneous dislocation distribution, i.e. also a dislocation cell structure, bears in it long-range internal stresses as a necessary consequence of strain compatibility, leading to internal forward stresses in the hard and internal back stresses in the soft regions, respectively. In order to develop the composite model further, some points need more work. First of all, there is a need to express the microstructural parameters of the composite model in terms of the macroscopic parameters measured in a mechanical test. Next, the composite model is a static consideration of the stress-applied state. It lacks all aspects of dislocation dynamics and thermal activation. It cannot, therefore, explain some other experimental observations such as, for example, the fact that the glide paths in stage II extend over, typically, 5 to 10 bundle/wall spacings. The idea of the composite model which considers the local stresses in soft and hard regions has consequences with respect to existing work-hardening models such as the long-range stress, the meshlength or the forest theories. These aspects will be discussed

9:00 AM
SEQUENCES OF DISLOCATION PATTERNS: *Frank R. Nabarro*[1]; [1]University of Witwatersrand, Johannesburg, Div. of Mats. Sci. and Tech. P.O. Box 395, CSIR, Pretoria 0001 South Africa

It is generally accepted that continued plastic deformation of a metal occurs in a sequence of stages. In each stage, the dislocation pattern shrinks, while remaining roughly self-similar, and the transition between successive stages is fairly abrupt. Possible causes for these changes of pattern are discussed. It is emphasized that the changes occur under an imposed stress. A simple model is presented in which, as the applied stress is increased through a critical value, a structure with a uniform dislocation density gives way to one with a higher average density but a lower total energy.

9:20 AM
DYNAMIC RECOVERY BY LOMER GLIDE: *Vasily V. Bulatov*[1]; Ali S. Argon[1]; [1]Massachusetts Institute of Technology, Dept. of Mech. Eng., Room 3-382, Cambridge, MA 02139 USA

Transition from stage II (linear hardening) to stage III (parabolic hardening) in FCC metals has been of considerable interest for decades. Although phenomenology of this transition is well established experimentally, its mechanistic interpretation remains an issue. Despite its wide acceptance, the well known Seeger's theory of dynamic recovery by cross-slip is not consistent with available experimental observations. We suggest a different mechanism for dynamic recovery in which dislocation density in the cell walls is reduced by recombination, concurrently with storage of new density. The recovery mechanism involves thermally-activated removal of the Lomer-Cottrell dislocation segments anchoring the excess dislocation density in the cell walls under the action of the applied stress and the active dislocation flux. Under normal conditions, in stage II, the LC locks are sessile, as is usually assumed. However, at higher stress levels typical of stage III deformation conditions, the locks can move in the {001} planes by the nodal glide mechanism discovered by Karnthaler[1]. Although nodal glide should be very slow compared to the motion of glissile dislocations, it provides a path for LC dislocation segment removal which will, in turn, trigger massive recombination of the excess dislocation density in the cell walls by spontaneous glide. We present results of large scale 3-D atomistic simulations of nodal glide in Al and Cu which demonstrate feasibility of the proposed scenario for dynamic recovery in stage III. [1]Karnthaler, H. P., 1978, Philos. Mag. A, 38, 141-156.

9:40 AM
BOUNDS AND INTERMEDIATE MODELING OF LARGE ELASTIC-VISCOPLASTIC BEHAVIOR OF POLYCRYSTALS: *Said Ahzi*[1]; [1]Clemson University, Dept. of Mech. Eng., Clemson, SC 29631 USA

The aim of this work is to propose a simple intermediate model for large elastic-viscoplastic deformations that could predict the copper and brass texture components in FCC metals as well as the texture transition. First, we propose a new formulation of the Sachs model as extension of this model to large elastic-viscoplastic deformations. In light of state variable based modeling, we introduce a one parameter weight function to formulate an intermediate model. This proposed model combines both bounds, Taylor and Sachs models. Our motivation for this investigation is to develop simple intermediate modeling other than the self-consistent models. In the applications, we concentrate on axisymmetric and plane strain compression tests. The results from all these models will be shown and compared with each other and with experimental results. A preliminary discussions concerning single parameter, used in the intermediate model, is given. This constitute a first attempt for modeling the effect of non-uniformity of deformation in polycrystals using simple intermediate modeling.

10:00 AM BREAK

10:15 AM INVITED PAPER
REALISTIC CONSTITUTIVE RELATIONS FOR METAL PLASTICITY: *U. Fred Kocks*[1]; [1]Los Alamos National Laboratory, Center for Materials Science, Mail Stop K765, Los Alamos, NM 87545 USA

In 1975, Ali Argon edited a book "Constitutive Equations in Plasticity". In it, two of the now widely acknowledged mainstays were presented: that plasticity must be expressed in state-variable form; and that different regimes of behavior exist that require different relations. Since then, this framework has been filled with a wide set of quantitative relations for a number of (mostly fcc) metals, with respect to both the kinetics of flow and the evolution of the state parameters in macroscopic bodies. The relations are not always expressible by closed-form equations, but by nomograms or graphs, derived by interaction with experiment and simulation. In this way, it is assured that the relations are actually executable in practice, and that they reflect real material behavior for a specific case. The most recent form of the underlying models will be given explicitly.

10:45 AM INVITED PAPER
A COMPARATIVE ANALYSIS OF LOW TEMPERATURE DEFORMATION IN B2 ALUMINIDES: NiAl, RuAl AND FeAl: *Tresa M. Pollock*[1]; David Lu[1]; Xiaoli Shi[1]; Khenlak Eow[1]; [1]Carnegie Mellon University, MSE Dept., 5000 Forbes Ave., Pittsburgh, PA 15213 USA

Aluminides with the B2 structure are an interesting group of compounds which could be useful as structural materials. However, these ordered compounds often lack adequate low temperature tensile ductility. In this study, macroscopic and microscopic aspects of deformation have been studied in a series of B2 aluminides with a wide range of melting temperature and varied levels of toughness and/or ductility. Deformation kinetics have been measured with the use of strain rate change experiments in the temperature range of 77K to room temperature. Dislocation substructures have been characterized in detail in critical regimes of temperature and strain rate. A wide variety of deformation processes have been observed, and their relationship to macroscopic properties will be discussed.

11:15 AM
DEFORMATION MICROSTRUCTURES IN SINGLE CRYSTALS AND POLYCRYSTALS AND WORK HARDENING STAGES: *N. Hansen*[1]; D. A. Hughes[2]; [1]Risoe National Laboratory, Mats. Research Dept., Roskilde DK-4000 Denmark; [2]Sandia National Laboratories, Center for Mats. and Applied Mechanics, Livermore, CA 94550 USA

The evolution of dislocation structures in single crystals and polycrystals with increasing strain is described within a framework of grain subdivision by dislocation boundaries and high angle boundaries. The microstructures evolving are characterized with emphasis on morphology and the changes in the misorientation across and the spacing between the deformation induced boundaries. These parameter changes are modelled over a large strain range using scaling methods of relevance to microstructural and micromechanical modelling. The dislocation boundaries are further analyzed using Franks formula. It is shown that the dislocations in the boundaries originate in part from active slip systems which are predicted by a Schmid factor analysis or a Taylor-Bishop-Hill model. In addition, these analyses show that supplementary slip systems are activated due to the presence of the deformation induced boundaries. These different types of analyses lead to a discussion of the mechanisms controlling the microstructural evolution and of correlations between the microstructural transformations and the work hardening stages.

11:35 AM
THE EFFECT OF PARTICLE DISTRIBUTION ON DEFORMATION AND DAMAGE IN TWO-PHASE ALLOYS: K. Conlon[1]; P. Poruks[1]; *D.S. Wilkinson*[1];J.D. Embury[1]; [1]McMaster University, Dept of Materials Science and Engineering, Hamilton, Ontario L8S 4L7

In materials containing large (>1 micron) particles, which strengthen by continuum load transfer from the matrix, a non-uniform particle distribution can have a profound effect on both strength and ductility. We have studied this using a combination of modelling (based on self-consistent analysis) and experiments (based on model materials). The models are best able to treat severe cases of clustering when an essentially bimodal distribution exists. These show that inhomogeneity enhances the efficiency of load transfer. However, this effect is negated once damage commences. The models have been tested against experiments involving powder processed Al-Cu alloys containing a bimodal distribution of CuAl2 particles, and against spherodized steels in which a bimodal carbide distribution can be introduced through thermomechanical processing. The tensile and compressive behavior of these materials is broadly consistent with the theory.

MILTON BLANDER INTERNATIONAL SYMPOSIUM ON "THERMODYNAMIC PREDICTIONS AND APPLICATIONS": High Temperature Experimentation

Sponsored by: Extraction & Processing Division, Process Fundamentals Committee, ASM International: Materials Science Critical Technology Sector, Thermodynamics & Phase Equilibria Committee
Program Organizers: Ramana Reddy, University of Alabama, Dept. of Met. & Mats. Eng., Tuscaloosa, AL 35487 USA; Dr. A. D. Pelton, Montreal, Quebec H3C3A7 Canada

Tuesday AM Room: 4
March 2, 1999 Location: Convention Center

Session Chairs: Robert A. Osteryoung, North Carolina State University, Dept. of Chem., Raleigh, NC 27695-8204 USA; Kjell Hagemark, STATOIL, Research Centre, Trondheim, Ranheimsveien 10 Norway

8:30 AM INVITED PAPER
HIGH-TEMPERATURE THERMOCHEMISTRY; FROM LIQUID ALLOYS TO MOLTEN SALTS: *Ole J. Kleppa*[1]; [1]James Franck Institute, The University of Chicago, 5640 S. Ellis Ave., Chicago, IL 60637 USA

This paper will begin with a historical part. It starts with the first calorimetric study of liquid alloys by Kawakami carried out at Tohoku University in 1927-30. It will then touch on the calorimetric work on intermetallic compounds of Kubaschewski and Walter in Germany, first published in 1939. A study of this paper in due course led the author to the development of his first high-temperature reaction calorimeter in 1952. This new calorimeter was used very extensively in studies relating

to low-melting liquid alloys in the 1950's. A fairly detailed review of this work on liquid alloys was presented to the ASM in the symposium on "Liquid Metals and Solidification" published in 1958. However, the author had spent 1956-57 as a Visiting Professor at his alma mater in Trondheim, Norway. His office in Trondheim was next door to that of Professor Hakon Flood, the founder of the Norwegian School of Molten Salt Chemistry. His many discussions with Professor Flood led the author to conclude that calorimetry of molt en salt mixtures would be a very desirable new enterprise. However, the calorimeter used in his work on liquid alloys was not very suitable for studies of molten salts. Fortunately, in the meantime Calvet and Prat had in 1956 published their new monograph "Microcalorimétrie". Development of a series of new Calvet type calorimeters for temperatures which ranged from 350°C to 1100°C provided the obvious solution to detailed calorimetric studies of molten salt mixtures, from liquid nitrates to liquid fluorides. A review will be presented of our work in this field.

9:10 AM

DEVELOPMENT OF LIYO2 AS A SOLID ELECTROLYTE FOR LITHIUM: Luis Yamarte[1]; Aniceta Skowron[1]; *Anthony Petric*[1]; [1]McMaster University, Dept. of Metall. and Mats. Sci., Hamilton, Ontario L8S 4L7 Canada

The properties of lithium yttriate were studied and the crystal structure of monoclinic LiYO2 was determined using neutron diffraction. The mobility of Li ions in the YO2 framework is discussed. A cell was devised to determine the activity of lithium in liquid alloys. The lithium yttriate electrolyte was prepared by solid state reaction of lithium carbonate and yttrium oxide. The cells were made by slip casting the electrolyte powder into tubes and sealing them to Y2O3 lids. The following cell configuration was used for both titration of lithium and measurement of the E.M.F.: (-)Ta/Li/LiYO2/Li-Zn(liq)/Ta (+). The activities of lithium in molten Li-Zn alloys at 823K show moderately negative deviations from Raoult's law over the composition range studied. LiYO2 was found to have good stability in both air and molten lithium environments.

9:30 AM

PHOSPHATE CAPACITIES OF CaO SLAGS: *Ramana G. Reddy*[1]; [1]The University of Alabama, Dept. of Metall. and Mats. Eng., P.O. Box 870202, Tuscaloosa, AL 35487-0202 USA

The phosphate capacity of slag is a measure of ability of a slag to remove phosphorous from molten alloy. The phosphate capacities of $CaO\text{-}CaF_2$ and $CaO\text{-}AlO_{1.5}$ slags were experimentally determined. The melts were equilibrated in a graphite crucible with CO-Ar mixtures and Ag-P alloys between 1450 and 1600°C. The phosphate capacities model for predicting C_{PO4} in slags "a priori" was developed. The predicted data are in very good agreement with the experimental capacity data. The phosphorous distribution ratio was calculated using the capacity data for slags.

9:50 AM

THERMODYNAMICS OF HYDROGEN ABSORPTION AND DESORPTION IN Pd-Rh-Co TERNARY ALLOYS: *David F. Teter*[1]; Dan J. Thoma[1]; [1]Los Alamos National Laboratory, MST-6 (Metallurgy), MS: G770, Los Alamos, NM 87545 USA

The effect of varying the Rh and Co compositions on the thermodynamics of hydrogen absorption behavior, hydride formation and decomposition, and hydrogen capacity of several Pd-Rh-Co ternary alloys has been investigated using pressure-composition (PC) isotherms. The trends in the thermodynamic properties of the alloys as a function of Rh and Co content will be correlated to x-ray diffraction measurements of the lattice parameters as well as other physical properties of the alloys. An empirical model, based on binary Pd-based alloys, has been developed which accurately predicts the thermodynamic properties of hydrogen solution, hydride formation and decomposition, and the hydrogen capacity of the ternary Pd-Rh-Co alloys. Also, the effects of cycling on the thermodynamic parameters will be presented. Results show that cycling decreases the enthalpy of hydride formation and slightly increases the enthalpy of hydride decomposition.

10:10 AM BREAK

10:30 AM

THERMODYNAMICS OF IRON AND EARTH'S CORE: *Surendra K. Saxena*[1]; Leonid S. Dubrovinsky[1]; Peter Lazor[1]; [1]Uppsala University, Earth Sciences, Geocentrum, Villavägen 16, Uppsala S-75236 Sweden

There are four well-known structural polymorphs of iron, namely alfa and delta (body centerd cubic), gamma (face centered cubic) and epsilon (hexagonal closest packed). The possible occurrence of a new iron phase was suggested by [(1)]; the evidence was indirect, obtained through laser heating of iron above pressures of about 40 gigapascal (GPa). We found that the FCC phase (face centered cubic), when heated in its stability field, is quenchable at high pressures. Using this technique, we determined that the structure of the quenched phase at high pressures is DHCP (double hexagonal closest packed). Several experiments done using in-situ heating and x-ray have now confirmed the presence of this new phase [(2)]. Although experimental data are sparse, it is possible to obtain a fairly quantitative thermodynamic description of all the iron phases and the double hexagonal closest packed (DHCP) beta iron. Earth's core beginning at depths of 2900 Km (133 GPa) and continuing to the center (6730 Km, 360 GPa) consists principally of iron. Until experiments become feasible on iron above 200 GPa, extrapolation of thermodynamic data on iron is necessary for the study of the core. The assessed data on iron is based on experimental data on a) melting to 200 GPa, b) the location of the triple point HCP-DHCP-FCC at 36 GPa and 1450K and c) the location of the triple point DHCP-FCC-melt close to 60 GPa and 2800K. If no other phase transition intervenes, the melting of beta-iron at 360 GPa takes place at temperatures less than 5000K, which constrains the temperature of Earth's center to be less than that. However there are some shock-wave data that cannot be easily reconciled with the current data obtained with the diamond-anvil cell technique unless there is yet another high P phase transition of the beta phase at about 200 GPa to increase the melting temperature by about 1000 at the center. A search for such a phase is now on. [1]S. K. Saxena, Shen, G. & Lazor, P. Science, 260, 1312-1314, (1993). [2]S. K. Saxena, L. S. Dubrovinsky and Häggkvist, P. Geophys. Res. Lett., 23, 2441-2444 (1996). [3]O.L. Anderson, Rev. Geophys. Suppl., 429-441, (1995).

11:10 AM

PROPERTIES OF MONAZITE (LaPO4) BASED CERAMICS: *Robert M. Housley*[1]; Peter E.D. Morgan[1]; and Janet Davis[1]; [1]Rockwell Science Center, 1049 Camino dos Rios, Thousand Oaks, CA 91360.

Successful development of oxidation resistant ceramics with good strength and toughness properties at high temperatures could increase the efficiency of energy generation, with consequent major economic and environmental advantages. Monazite has a number of properties which suggest that it will be a valuable component in high temperature ceramic composites. Monazite-La (LaPO4) melts at 2074 C and is phase compatible with alumina and alumina based fibers to at least 1600 C. It is also soft and readily deforms by cleavage, twinning, and dislocation motion to quite low temperatures. Fiber pullout has been well documented. For these reasons we have been studying the synthesis of monazite and the fabrication of monazite based ceramics. Most synthesis methods yield a phosphorus rich product. Ceramics made from materials containing even a fraction of a percent excess phosphorus frequently exhibit giant grain growth and have little strength. We have developed a procedure for making stoichiometric monazite powder precursor. Ceramics made from it remain fine grained and tough even at high temperatures. Microstructures will be compared.

11:30 AM

MODELLING STUDIES IN MOLTEN SALT ELECTROREFINING OF PLUTONIUM: *B. Mishra* [1]; D.L. Olson[1]; A. Raraz[2]; [1]Kroll Institute for Extractive Metallurgy, Dep't. Metallurgical and Materials Engineering, Colorado School of Mines, Golden, CO 80401; [2]CMT 205, Argonne National Laboratory, 9700 S. Cass Avenue, Argonne, IL 60439-4837

The study and optimization of process parameters in some of the processes involved in the production of plutonium metal is extremely difficult. Due to the dynamic nature of the systems operating at high temperatures under protective atmospheres, safety and health-hazard concerns, waste-related issues and the cost considerations, the use of actinide metals directly to investigate the processes is inappropriate. This study discusses the use of various metals and alloys to simulate the

pyrometallurgical characteristics of plutonium. Design parameters relating to component arrangement in process-reactors, process parameters relating to chemical behavior of plutonium and operating parameters relating to reactor conditions, such as the temperature, stirring, current density, metal recovery, etc. have been studied through modeling. The validity and justification of these measurements have been discussed.

11:50 AM

EXPERIMENTS IN THE REMOVAL OF COPPER FROM IRON WITH OXIDE AND SULFIDE-MODIFIED OXIDE FLUXES: *Adam Cohen*; Argonne National Laboratory, 9700 S. Cass Ave., ET/Bldg 212, Argonne, IL 60439-4838.

If an economically viable method were available for removing copper from scrap iron, steelmakers could turn high-copper-content scrap (above 0.1 wt.%) into useful products. Molten salt mixtures of charge-asymmetric cation species show a significant drop in the activity coefficient for monovalent cation species in the presence of trivalent or higher cation species. This phenomenon can be used to design a flux for the removal of copper as a (monovalent) cuprous species from iron-based metal. Distribution coefficients of copper (i.e., the ratio of the weight percent copper in a matte to that in the metal) have been determined by various authors between a sulfide flux and iron. However, the values have not been high enough to make their use on a commercial scale economically viable, largely because a sulfide flux would result in a high sulfur content in the treated metal. A sulfide-based process would likely need a distribution coefficient of 100 or higher to be a good candidate for a commercial process. In this study, experiments were conducted to determine if distribution coefficients between an oxide flux (consisting of alumina, silica, calcia, and ferrous oxide) and iron would be increased by the charge-asymmetric effect described above. In the limited number of tests conducted, a maximum distribution coefficient of 0.5 was found at 1,923 K. While this distribution coefficient is significantly higher than the equilibrium constant required for the reaction between ferrous oxide and copper to form cuprous oxide (K » 0.025), it is not high enough for the process to be developed commercially. Finally, distribution coefficients were determined between a sulfide-modified oxide flux (consisting of alumina, silica, ferrous sulfide, and dilute amounts of calcia, magnesia, calcium sulfide, or magnesium sulfide) and iron with various concentrations of carbon at 1,823 K. A maximum distribution coefficient for copper of 6.8 was found for iron with 0.1 wt.% carbon; distribution coefficients increased as carbon content decreased. While that level is still too low for commercial applications, further research with the mixed flux is strongly recommended because significantly higher distribution coefficients should be possible.

11:50 AM

RARE EARTH CONTAINING HALIDE SOLUTIONS AND PHASE DIAGRAM DETERMINATION: *Zhiyu Qiao*[1]; [1]University of Science & Technology Beijing, Dept. of Phys. Chem., Beijing 100083 China

China is very rich in rare earths (RE). Fundamental research work on RE containing halide solution models and phase diagram determinations is of great importance for better understanding their structures and properties as well as for RE applications. As a key project supported by the National Natural Science Foundation of China in cooperation with CRCT, Ecole Polytechnique de Montreal, Canada, RE containing halide solution models have been studied and the phase diagrams of the RE halide and divalent iodide systems have been determined by the CALPHAD technique in combination with accurate experimental measurements. Several models for describing the Gibbs energies of RE liquid halide solution, especially the polynomial series in equivalent fractions and a modified quasichemical theory developed by M. Blander and A. Pelton, are discussed for phase diagram optimization. Several series of binary RE containing halide and divalent iodide phase diagrams have been optimized and calculated, agreeing with experimental data quite well. As well, a series of ternary phase diagrams of the RE containing chloride systems has been successfully predicted by using the FACT system. In order to determine reliable measured phase diagram, many experimental improvements have been made and are also discussed. (Project supported by National Natural Science Foundation of China.)

MINIATURE STRUCTURES & COMPONENTS UNDER CYCLIC LOADING; FATIGUE & INTERNAL FRICTION: Session I

Sponsored by: Structural Materials Division, Non-Ferrous Metals Committee; Electronic, Magnetic & Photonic Materials Division, Electronic Packaging and Interconnection Materials Committee; ASM International: Materials Science Critical Technology Sector, Flow & Fracture Committee

Program Organizers: H. D. Merchant, Gould Electronics, Inc., Eastlake, OH 44095-4001 USA; Thomas R. Bieler, Michigan State University, Dept. of Mats. Sci. & Mech., East Lansing, MI 48824-1226 USA; James C. Earthman, University of California, Dept. of Chem. Eng. & Mats. Sci., Irvine, CA 92717-2535 USA; M. Wuttig, University of Maryland, Dept. of Mats. & Nuclear Eng., College Park, MD 20743-2115 USA

Tuesday AM Room: 11B
March 2, 1999 Location: Convention Center

Session Chair: James Earthman, University of California - Irvine, Dept. of Chem. Eng. and Mats. Sci., Irvine, CA 92717-2535 USA

8:30 AM INVITED PAPER

RESIDUAL STRESSES AND THERMOMECHANICAL FATIGUE RESPONSE IN MINIATURE STRUCTURES AND COMPONENTS: *Subra Suresh*[1]; [1]Massachusetts Institute of Technology, Dept. of Mats. Sci. and Eng., 77 Massachusetts Ave., Room 4-140, Cambridge, MA 02139-4307 USA

The measurement of residual stresses and thermomechanical fatigue characteristics of small-volume structures and components will be examined. Theoretical, computational and experimental results for extracting the magnitude and sign of residual stresses in thin films and surface layers of thick materials will be presented. Independent and complementary experimental methods for the extraction of plastic yield properties of thin films and patterned thin lines on substrates will then be considered by recourse to curvature measurements, nanoindentation and x-ray diffraction. Theoretical formulations which facilitate the determination of curvatures, volume-averaged stresses and/or thermal fatigue loading conditions for the onset of plastic yielding will then be considered along with experimental results for glass, aluminum and copper films/lines on silicon substrates. The effects of microstructural, crystallographic, and physical size effects on the interpretation of various properties will also be highlighted.

9:10 AM INVITED PAPER

MECHANICAL FATIGUE OF THIN COPPER FOIL: *Harish D. Merchant*[1]; Melvin G. Minor[1]; Y. N. Liu[2]; [1]Gould Electronics, 34929 Curtis Blvd., Eastlake, OH 44095-4001 USA; [2]University of Kentucky, Light Metals Laboratory, Anderson Hall, Lexington, KY USA

Copper foils, 12um to 35um thick, are subjected to the bending/unbending fatigue around a mandrel in the flex and fold modes. Electrodeposited and rolled foils are employed. The strain-based fatigue is evaluated over a wide range of strain amplitudes. The fatigue life versus strain amplitude curve in the high strain amplitude (low cycle) and low strain amplitude (high cycle) regimes is developed for each foil type prior to and following recrystallization anneal. The parameters of Coffin-Manson relationship are utilized to calculate the cyclic strain hardening parameter and fatigue ductility. The initiation and propagation of fatigue crack through the foil thickness and across the sample width are related to the unique fine grain structure for each foil type, pancaked grains for the rolled foil and equiaxed grains for the electrodeposited foil. The variations in electrical resistance, microhardness, grain structure and dislocation structure with fatigue are monitored. The fatal

fatigue failure is associated with an increase in electrical resistance beyond a preassigned threshold which corresponds with the convergence of through-thickness and across-the-width fatigue crack.

9:40 AM INVITED PAPER

A DYNAMIC MODEL FOR SOLDER AND THE PROBLEM OF ACCELERATED LIFE TESTING: *Stan Russell*[1]; Anne Gringals[1]; Ed Clemente[1]; [1]Motorola, Space and Systems Technology Group, 8220 E. Roosevelt St., Scottsdale, AZ 85252 USA

Solder joint reliability under thermal cycling is a key problem in electronic packaging. Accelerated life testing (few cycles larger temperature excursions) is a practical necessity in predicting fatigue life in field environments (many cycles, smaller temperature excursions). Complex solder behavior with marked temperature dwell and cycle time influence at slower frequencies makes this a difficult problem. A dynamic model is presented which couples micro instability of coarsened grain band evolution with changes in macroscopic constitutive behavior. Key features of the model include effects of shear band width to total solder joint thickness, pertinent to small scale design, and frictional resistance at slow load rates. Model fit and interpretation of published data are discussed as well as implications for accelerated life test design.

10:10 AM BREAK

10:20 AM INVITED PAPER

AUTOMATED INSTRUMENTATION FOR DETERMINING THE DAMPING CAPACITY OF MATERIALS AND SMALL STRUCTURES: *James C. Earthman*[1]; [1]University of California - Irvine, Dept. of Chem. and Biochem. Eng. and Mats. Sci., Irvine, CA 92697-2575 USA

Novel instrumentation interfaced to a percussion probe will be presented that can quantitatively determine the damping capacity of material samples and structures including biomedical implant components. The loss coefficient is used to characterize mechanical damping capacity of a material or structure. Values of this property for dental prostheses will be presented and compared with those for natural teeth. It will be shown how these values may be used to evaluate mechanical integrity as well as being used in the assessment and design of prosthetic structures. A further assessment of the measured stress wave response of small structures will also be discussed.

10:50 AM INVITED PAPER

AFM ANALYSIS OF CUMULATIVE FATIGUE DAMAGE IN CU THIN FILMS: Donald Kramer[1]; Alex Volinsky[1]; Gina Sandvick[1]; Yosef Katz[2]; William Gerberich[1]; [1]University of Minnesota, Chem. Eng. and Mats. Sci., 151 Amundson Hall, 421 Washington Ave. SE, Minneapolis, MN 55455 USA; [2]Nuclear Research Center, POB 9001, Negev, Beer-Sheva 84190 Israel

Established techniques for evaluation of slip-step evolution in bulk copper have been applied to micron size thin copper films. Sputter deposited copper films on titanium substrates have been annealed from 230ϒC to 310ϒC and reverse-bend fatigue cycled. Damage rates are identified as the fraction of accumulated plastic strain emerging at the free surface measured by atomic force microscopy. These are compared to bulk samples of copper which have been cold worked and annealed to corresponding temperatures. While the bulk samples can be interpreted in terms of a microstructurally-based low-cycle fatigue law, constraint by the substrate requires additional insight to model thin film behavior. Possible micromechanisms are discussed.

NONDESTRUCTIVE EVALUATION (NDE) AND MATERIAL PROPERTIES IV: Nondestructive Evaluation (NDE) and Material Properties Session III

Sponsored by: Jt. ASM International: Materials Science Critical Technology Sector, Structural Materials Division, Nuclear Materials Committee

Program Organizers: Peter K. Liaw, University of Tennessee, Dept. of Mats. Sci. & Eng., Knoxville, TN 37996-2200 USA; Richard J. Arsenault, University of Maryland, Nuclear Eng. Bldg., College Park, MD 20742-2115 USA; Robert E. Green, The John Hopkins University, Baltimore, MD 21218-2689 USA; K. Linga Murty, North Carolina State University, P.O.CBox 7909, Raleigh, NC 27695-7909 USA; R. Thompson, Iowa State University, Ames Laboratory, Ames, IA 50011 USA

Tuesday AM Room: 16A
March 2, 1999 Location: Convention Center

Session Chairs: K. L. Murty, North Carolina State University, Dept. of Mats. Sci. and Eng., Raleigh, NC 27695-7909 USA; Thomas J. Mackin, University of Illinois, Dept. of Mech. and Indust. Eng., Urbana, IL 61801 USA

8:30 AM INVITED PAPER

NON-DESTRUCTIVE EVALUATION OF THE EFFECT OF AGING ON TENSILE PROPERTIES OF ALLOY 625: *M. D. Mathew*[1]; K. L. Murty[1]; K. B. S. Rao[2]; S. L. Mannan[2]; [1]North Carolina State University, Dept. of Nuclear Eng., Raleigh, NC 27695-7909 USA; [2]Indira Gandhi Centre of Atomic Research, Mats. Development Division, Kalpakkam, TN 603 102 India

The effect of aging on the tensile properties of Alloy 625, a solid solution strengthened nickel base superalloy, was investigated using the non-destructive Stress-Strain Microprobe (SSM) system. SSM is based on automated ball indentation (ABI) technique, and involves strain-controlled multiple indentations by a small spherical indenter at a single penetration location on the material surface. The technique permits evaluation of tensile deformation parameters such as yield strength, ultimate tensile strength, strength coefficient and strain hardening exponent, as well as elastic-plastic fracture toughness parameter Kjc. Alloy 625 was aged at six different temperatures in the range of 873 to 1173K for 500 hours each. ABI tests were carried out at room temperature and at 473K. The variation of yield and ultimate tensile stresses with aging temperature showed a peak in strength at 973K. The peak stress was two times the strength of the unaged material, whereas the strength after aging at 1173K was nearly equal to that of the unaged material. Microstructural studies showed that the peak in strength resulted from the precipitation of "g" precipitates. The fall in strength due to aging above 973K is attributed to the precipitation of d-phase. ABI is a non-destructive testing technique to determine changes in mechanical properties of materials and components due to aging.

9:00 AM

THE APPLICATION OF PASS THROUGH FLUX FOR NON-DESTRUCTIVE TESTING AND PROCESSING CONTROL OF MAGNETIC SPUTTERING TARGETS : *Hao Zhang*[1]; Jeff Hart[1]; Tim Newport[1]; [1]Tosoh SMD, Inc. , R&D, 3600 Gantz Rd., Grove City, OH 43123 USA

The magnetic permeability and its consistency are the key factors determining the performance of a magnetic sputtering target. The performance of a magnetic target can be significantly improved by decreasing the magnetic permeability and increasing the pass through

flux (PTF), which measures the magnetic field transmitted through a ferromagnetic material. Typically, magnetic permeability is measured on miniature samples by destructive methods. It is inapplicable to measure permeability and its consistency for every target, particularly in manufacturing. In this paper, the correlation among the magnetic permeability, PTF, target thickness, crystallographic texture and fabrication process of Co targets was studied. The permeability and PTF of the Co targets fabricated by different processes were measured, and the 3-D PTF mapping was constructed to show its consistency across the targets. The results showed that the permeability strongly depended on fabrication process, microstructure and texture. The PTF increased with decreasing permeability. By control the microstructure and texture of the Co targets through processing, the permeability and PTF can be optimized. The application of the PTF for non-destructive testing and in-situ processing control in manufacturing was also studied. It has demonstrated that the PTF testing is an effective NDT tool in determining the magnetic properties, microstructure, texture and their consistency in manufacturing, and is an effective tool for quality control.

9:30 AM INVITED PAPER

ESTIMATING FATIGUE LIFETIMES OF DAMAGED COMPOSITES USING THERMOELASTICITY: *Gavin P. Horn*[1]; Peter Kurath[1]; Thomas J. Mackin[1]; [1]University of Illinois, Mech. and Industrial Eng., 140 MEB, 1206 W. Green St. MC 244, Urbana, IL 61801 USA

A new experimental method is presented for quantifying impact damage in composites, rationalizing fatigue data following impact, and for estimating the current state and remaining lifetime in composite materials. The procedure was demonstrated using samples of randomly oriented, continuous glass fiber reinforced polyurethane and epoxy. Composite samples were impact-damaged using an Instron/Dynatup 8250 Drop Tower system. Thermoelastic stress analysis (TSA) was then used to quantify the impact damage by assigning a stress concentration factor to the damaged site. Following impact and TSA imaging, the samples were fatigued to failure using a range of stress amplitudes. The stress concentration factors measured using TSA provided a rational understanding of the resulting fatigue lifetimes. Stress-life predictions were made for a significant range of damage over three decades of life, displaying a correlation coefficient closely resembling that of baseline, unimpacted specimens. In addition, the thermoelastic method was used to detect damage induced by machining test samples. These tests demonstrated the general utility of TSA as a non-destructive method for imaging and quantifying composite damage.

10:00 AM

DYNAMIC MODULUS AND POISSON RATIO MEASUREMENT OF Ti/TiB COMPOSITES BY IMPULSE EXCITATION: *Revti R. Atri*[1]; K. S. Ravichandran[1]; [1]University of Utah, Dept. of Metall. Eng., 135 S 1460 E Rm. 412, Salt Lake City, UT 84112 USA

The elastic modulus, shear modulus and the Poisson ratio of four different Ti-TiB composites, along with monolithic Ti and TiB were measured using the impulse excitation of vibration technique. This dynamic test method is specifically appropriate for the material being studied and requires the use of simple operating procedures. Most importantly this method can be used on geometrically simple specimens and is non-destructive in nature. Three specimens of Ti, TiB and Ti-TiB composites of size 60X15X3mm were cut by EDM. The Ti-TiB composite compositions consisted of Ti-20TiB, Ti-40TiB, Ti-60TiB, and Ti-80TiB. The elastic modulus for monolitic Ti and TiB were 116.8 and 426.0, respectively. In the composite materials there was an increase in elastic modulus and shear modulus with increasing volume fraction of TiB. The average shear modulus for monolithic Ti and TiB were 44.1 and 185.4, respectively. The Poisson ratio value was 0.32 for monolithic Ti and 0.15 for TiB and decreased with increasing volume fr action fo TiB in the composite materials. The values of elastic modulus measured from impulse excitaion were in good agreement with experimental data.

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 USA

Tuesday AM Room: 5B
March 2, 1999 Location: Convention Center

Session Chairs: John N. Hryn, Argonne National Laboratory, Energy Systems Div., Argonne, IL 60439 USA; James A. Sommers, Oremet Wah Chang, Albany, OR 97321 USA

8:30 AM

SYNTHESIS OF INTERMETALLIC COMPOUNDS BY REDUCTION OF MULTICOMPONENT SOLUTIONS OF LIQUID AMMONIA: *Hongmin Zhu*[1]; Donald R. Sadoway[1]; [1]Massachusetts Institute of Technology, Dept. Mats. Sci. and Eng., 77 Massachusetts Ave., Rm 8-109, Cambridge, MA 02139-4307 USA

Sodium dissolves in liquid ammonia to give Na^+ and a solvated electron. The result is a medium that is very potent for metallothermic reduction. The production of tantalum powder by reaction of a solution of $TaCl_5$ dissolved in liquid ammonia with a solution of Na dissolved in liquid ammonia has been demonstrated. Beyond this, co-precipitation/co-reduction of metals by first dissolving multiple compounds of the metals in liquid ammonia and then reducing the solution to promote the precipitation of mixed metal product has been demonstrated. Various intermetallic compounds have been produced in this manner. Sponsorship of the research from Cabot Performance Materials is gratefully acknowledged.

8:55 AM

APPLICATION OF LITHIUM IN MOLTEN SALT REDUCTION PROCESSES: *K. V. Gourishankar*[1]; E. J. Karell[1]; [1]Argonne National Laboratory, Chemical Technology Division, 9700 S. Cass Ave., Argonne, IL 60439 USA

At the Argonne National Laboratory (ANL), we have developed a pyrochemical process that uses lithium to reduce oxide spent nuclear fuel. The reduction is carried out at 650°C in a molten salt (LiCl) bath. Li_2O, produced during the reduction of the fuel, dissolves in the molten salt. At the end of the reduction step, the lithium is regenerated from the salt by an electrowinning process. The lithium and the salt from the electrowinning step are then reused for reduction of the next batch of oxide fuel. The process cycle has been successfully demonstrated on a large-scale in a specially designed pyroprocessing facility. The process demonstrates the applicability of lithium as a reductant in a molten salt system and can be adapted for the extraction of other metals. An important feature of this process is that the salt and the lithium are recycled for use in the next reduction cycle. This presentation will describe the role of lithium in molten salt reduction processes with specific reference to our process that has been developed for the reduction of actinide oxides in spent nuclear fuel.

9:20 AM

A SPECTROSCOPIC AND ELECTROCHEMICAL STUDY OF TITANIUM ELECTROREFINING: *Luis Ortiz*[1]; Donald R. Sadoway[1]; [1]Massachusetts Institute of Technology, Dept. Mats. Sci. and Eng., 77 Massachusetts Ave., Rm 8-109, Cambridge, MA 02139-4307 USA

Metallothermic reduction of $TiCl_4$ produces commercial grade titanium in the form of sponge. For microelectronics applications, high-purity metal can be produced from sponge by electrorefining in a melt composed of chlorotitanates dissolved in alkali chlorides. The relevant physical chemistry of the electrorefining process is under investigation. Melt chemistry is being studied by Raman spectroscopy. Electrode reactions are being studied by various transient techniques including a.c. voltammetry and electrochemical impedance spectroscopy. Electrolysis trials are being conducted in laboratory-scale cells. Recent results will

be reported in conference. Sponsorship of the research from The ALTA Group, a Johnson Matthey company, is gratefully acknowledged.

9:45 AM
SENSORS FOR USE IN SYSTEMS CONTAINING MULTIPLE REACTIVE METALS: *Jeffrey W. Fergus*[1]; [1]Auburn University, Mats. Research and Education Center, 201 Ross Hall, Auburn University, AL 36849 USA

Many reactive metals form ionic compounds that can be used as electrolyte or electrode materials in electrochemical sensors. Such sensors can conveniently be used to measure the concentration of a particular reactive element in a non-reactive environment. When multiple reactive elements are present, however, competitive exchange reactions can occur and lead to instability of the sensor and/or mixed response of the sensor. In this paper, some of the issues and approaches involved in developing sensors for use in systems containing multiple reactive metals will be discussed. Examples include magnesium + strontium or magnesium + sodium in molten aluminum, antimony in molten zinc and barium + cesium vapor.

10:10 AM BREAK

10:20 AM
PRODUCTION OF Ti-Al ALLOY-ALUMINA COMPOSITE PARTICLES: *P. C. Maity*[1]; [1]National Institute of Foundry and Forge Technology, Foundry Technology Dept., P.O. Hatia, Ranchi, Bihar 834 003 India

Titanium dioxide (TiO_2) particles (2 wt.%) were incorporated into commercially pure aluminum melt at 700°C by vortex method. After complete addition of the particles, the melt was treated with 0.3 wt.% hexachloroethane to extract the reaction products of Al and TiO2. The extracted particles contained Ti - 37%, Al - 15% and Al_2O_3 - 48% approximately.

10:45 AM
SYNTHESIS AND CASTING OF A LITHIUM-BISMUTH COMPOUND FOR AN ION-REPLACEMENT ELECTROREFINER: *Sean M. McDeavitt*[1]; [1]Argonne National Laboratory, Chemical Technology Division, 9700 S. Cass Ave., Argonne, IL 60439 USA

Recent ion replacement electrorefining experiments at ANL required the lithium-bismuth intermetallic Li_3Bi. Approximately 3.5 kg of Li_3Bi were synthesized using a high-temperature induction casting furnace. Small-scale (20 g) experiments were used to develop the synthesis method. Four larger-scale castings (500 to 1250 g) were completed by combining high purity lithium and bismuth in a tantalum crucible. Pure Li and Bi metals have relatively low melting points (Li: 180.5°C, Bi: 271.3°C), but the intermetallic has a relatively high melting point (1145°C). The metals were heated slowly to melt the charge. Upon melting of the bismuth, the formation reaction (3Li + Bi -> Li_3Bi) proceeded vigorously and the furnace power was temporarily turned off at this time. After several minutes, the tantalum crucible would stop glowing and the furnace temperature would be increased to 1200°C to melt and homogenize the compound. Liquid Li_3Bi was cast into cold stainless steel molds.

11:10 AM
MICROSTRUCTURAL DEVELOPMENT AND EVOLUTION IN UAlx, U-Al-Si, AND U-Al-Ca-O ALLOYS FOR THE DISPOSITION OF DOE SPENT NUCLEAR FUELS: *Thad M. Adams*[1]; Harold B. Peacock[1]; Fred C. Rhode[1]; Natraj C. Iyer[1]; [1]Westinghouse Savannah River Company, Savannah River Technology Center, Bldg. 773-41A, Rm. 151, Aiken, SC 29808 USA

The melt-dilute treatment technology program is focused on the development and implementation of a treatment technology for diluting highly enriched (>20% ^{235}U) aluminum spent nuclear fuel to low enriched levels (<20% ^{235}U and qualifying the LEU SNF form for geologic repository storage. In order to reduce the enrichment of these assemblies prior to ultimate geologic repository disposal, the melt-dilute technology proposes to melt these SNF assemblies and then dilute with additions of depleted uranium. The emphasis within the development program to date has been on determining the process definition and basis, developing process cycle options, and demonstrating the versatility and adaptability of the process for the treatment of all types of U-Al SNF (UAl_x, Al-U_3O_8, and Al-U_3Si_2). In determining the process definition and basis a wide range of alloys, representative of those expected in the SNF form, have been fabricated an d their product characteristics, namely microstructure, homogeneity, phase composition, etc. have been analyzed using SEM/EDS and XRD. The development of ternary isothermal sections for the U-Al-Si system using the standard Gibbs triangulation technique with validation from experimental solidification and dissolution data has been performed. Lastly, thermodynamic calculations assessing the possible reaction paths in the U-Al-O system with additional dissolution kinetics experiments using depleted U_3O_8 and Al or Al-Ca alloys have been conducted with the Al-Ca alloy being more effective at U_3O_8 reduction. Additionally, partitioning during alloy solidification of the radionuclides species (Cs, Tc, Pd, Sr, Zr, Mo, Y, Ce, Se, Te) which are present from the fission process in minor concentrations has been investigated as well as the microstructural and phase evolution of these alloys under repository storage conditions.

11:35 AM
MICROSTRUCTURE OF THE ZIRCONIUM-8 WT% STAINLESS STEEL ALLOY: *Daniel P. Abraham*[1]; James W. Richardson[2]; [1]Argonne National Laboratory, Chem. Tech. Div., Bldg. 205, Room A167, 9700 S. Cass Ave., Argonne, IL 60439 USA; [2]Argonne National Laboratory, Intense Pulsed Neutron Source, 9700 S. Cass Ave., Argonne, IL 60439 USA

The Zirconium-8 wt% Stainless Steel (Zr-8SS) alloy is being developed by Argonne National Laboratory as a metal waste form to contain radioactive isotopes isolated from metallic spent nuclear fuel. The microstructure of the Zr-8SS alloy has been examined by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). The lattice parameters and volume contents of phases have been obtained by neutron diffraction. The major phase in the as-cast alloy is α-Zr; small amounts of the $Zr_3(Fe,Ni)$, $Zr_2(Fe,Ni)$, $Zr_2(Fe,Cr)$ and $Zr(Fe,Cr)_2$ intermetallics are also present in the alloy. On heat treatment, the amount of α-Zr, $Zr_2(Fe,Ni)$ and $Zr_2(Fe,Cr)$ decreases, whereas the amount of $Zr_3(Fe,Ni)$ and $Zr(Fe,Cr)_2$ increases. The relative stabilities of the various phases will be discussed with reference to the Zr-Fe phase diagram.

STRUCTURAL SILICIDES: Processing, Mechanical Properties, Precipitation

Sponsored by: Jt. ASM International: Materials Science Critical Technology Sector, Structural Materials Division, Corrosion and Environmental Effects Committee; ASM International: Materials Science Critical Technology Sector, Mechanical Behavior of Materials Committee

Program Organizers: J.H. Schneibel, Oak Ridge National Laboratory, Metals & Ceramics Div., Oak Ridge, TN 37831 USA; Michael J. Kaufman, University of Florida, Dept. of Mats. Sci & Eng., Gainesville, FL 32611-2066 USA; Matthew J. Kramer, Iowa State University, Ames Laboratory, Ames, IA 50011 USA

Tuesday AM — Room: 16B
March 2, 1999 — Location: Convention Center

Session Chairs: C. T. Liu, Oak Ridge National Laboratory, Metals and Ceramics Div., Oak Ridge, TN 37831-6115 USA; J. Mundy, 10720 Game Preserve Road, Gaithersburg, MD 20879-3106 USA

8:30 AM INVITED PAPER
A REVIEW OF NIOBIUM SILICIDE-BASED IN-SITU COMPOSITES: *B. P. Bewlay*[1]; M. R. Jackson[1]; [1]GE Corporate Research and Development, Niskayuna, NY 12309 USA

This paper will describe processing and properties of high-temperature Nb silicide based in-situ composites. These composites consist of

high-strength Nb-based M_3Si and M_5Si3 silicides together with a modest strength, high-toughness Nb-based metallic phase. Preliminary in-situ composites were derived from the binary Nb- Nb_3Si eutectic and Nb Nb_5Si_3 eutectoid reactions. While these composites displayed an attractive balance of high- and low-temperature mechanical properties, they possessed very poor environmental resistance. In order to obtain a more complete balance of properties, the more recent composites are derived from higher order alloys that contain additions such as such as Ti, Hf, Mo, Al and Cr. These in-situ composites have been produced by a number of approaches including arc melting, direction solidification, and physical vapor deposition. The role of secondary processing operations, such as extrusion and forging, has also been studied. This paper will describe composite microstructures, room-temperature fracture toughness and elevated-temperature property data (tensile strength, creep performance, and oxidation behaviour). These composites have promising high-temperature strength and oxidation resistance at temperatures of 1315ϒC (2400F) when compared with other intermetallic-based systems. The high temperature mechanical properties and oxidation behavior will be also compared with the most recent Ni-based superalloys.

9:00 AM INVITED PAPER

AN OVERVIEW ON THE PROCESSING OF MOLYBDENUM SILICIDES AND THEIR COMPOSITES: *S. C. Deevi*[1]; [1]Philip Morris USA, Development and Eng. Center, Richmond, VA 23234 USA

Silicides based on molybdenum have received considerable attention as opposed to the other structural ceramics due to their excellent oxidation resistance, and ductility at high temperatures. Silicides allow incorporation of reinforcements, and are stable with many additives even at high temperatures allowing the process engineer to design a structural ceramic utilizing the unique metallic properties of molybdenum silicides. In this paper, we present the processing methodologies adopted for the processing of molybdenum silicides using Mo and Si powders to obtain $MoSi_2$, Mo_5Si_3, and other composites, and compare them with the conventional techniques such as casting, hot pressing and hot-isostatic pressing. An attempt will be made to generalize the features of processing among the different techniques, and their effect on the fracture toughness, oxidation strength, pesting, and high temperature creep of the silicides. In addition, we will also present the unique aspects of composites based on $MoSi_2$-Si_3N_4 composites, and the processing challenges involved to make the composites a commercial reality.

9:30 AM INVITED PAPER

DEVELOPMENT OF MOLYBDENUM SILICIDES + MOLYBDENUM COMPOSITES FOR HIGH-TEMPERATURE STRUCTURAL APPLICATIONS: *M. G. Mendiratta*[1]; P. R. Subramanian[1]; T. A. Parthasarathy[1]; J. Simmons[1]; R. Wheeler[1]; D. Dimiduk[2]; [1]UES, 101-000, 4401 Dayton-Xenia Rd., Dayton, OH 45432 USA; [2]Air Force Research Laboratory, Mats. and Manufact. Directorate, AFRL/MLLM, Wright-Patterson AFB, OH 45433 USA

Research is in progress on the Mo_5SiB_2 + Mo_3Si + α-Mo in-situ composites for structural applications in the 800-1400ϒC temperature range. Composites of various compositions are prepared by casting of small buttons for investigations of phase relations, microstructural evolution and oxidation behavior. Large cast billets are hot-extruded for mechanical property determinations. The mechanical behavior studies include measurements of toughness, strength, ductility and creep from room temperature to 1400ϒC. In addition, alloying studies are in progress involving additions of Cr, V, Nb, W, Ge, and Al to alter the equilibrium phases to improve oxidation resistance. Results will be presented and discussed in relation to other high-temperature material systems currently under development for structural applications. UES, Inc.; Research being performed under Contract F33615-96-C-5258.

10:00 AM BREAK

10:20 AM

FORMATION OF SILICIDE PRECIPITATES IN Nb-Si-BASED IN-SITU COMPOSITES: *B. P. Bewlay*[1]; R. J. Grylls[2]; H. L. Fraser[3]; [1]GE Corporate Research and Development, 1 Research Circle, Schenectady, NY 12309 USA; [2]GE Aircraft Engines, 1 Neumann Way, Cincinnati, OH 45215 USA; [3]The Ohio State University, Dept. of Mats. Sci. and Eng., Columbus, OH 43210 USA

In-situ composites based on Nb-Si alloys are being considered as future materials for high- temperature structural applications. The directionally-solidified in-situ composites studied in this work possess a microstructure consisting of dendrites of a niobium solid solution, surrounded by a eutectic mixture of niobium and Nb_3Si. In both the as-cast and heat-treated conditions, precipitates are observed within the niobium dendrites, and the object of this paper is to provide a detailed characterization of these precipitates, both in binary and higher-order hypoeutectic alloys. It is found that the precipitates have the Nb_3Si stoichiometry, but they do not possess the stable Nb_3Si crystallography. The precipitates possess a metastable orthorhombic crystal structure which is related to the niobium matrix via a simple orientation relationship. The precipitates are typically seen as semi-coherent faceted needles, with dimensions ranging from 2nm to several microns, depending on the heat-treatment. It will be shown that the precipitates form on cooling from the heat-treat temperature due to the reduction in Si solubility in the niobium on cooling. Hardness data indicate that these precipitates provide some strengthening of the niobium matrix, and the possibility for using these precipitates as a strengthening phase will be discussed.

10:40 AM

OBSERVATIONS OF THE FRACTURE BEHAVIOUR OF Nb-Si IN-SITU COMPOSITES USING CROSS-SECTIONAL ELECTRON MICROSCOPY: *Bernard P. Bewlay*[1]; R. J. Grylls[2]; H. L. Fraser[3]; [1]GE Corporate Research and Development, 1 Research Circle, Schenectady, NY 12309 USA; [2]GE Aircraft Engines, 1 Neumann Way M85, Cincinnati, OH 45215 USA; [3]The Ohio State University, Dept. of Mats. Sci. and Eng., Columbus, OH 43210 USA

Composites based on Nb-Si alloys are attractive candidates for use as structural materials at the very high temperatures required for future generation aircraft engines. Binary Nb-Si alloys are limited by their low room-temperature fracture toughness, but in-situ composites have been developed which have fracture toughness values of > 20 $MPam^{1/2}$. In this study the fracture behavior of a range of in-situ composites has been investigated using cross-sectional transmission electron microscopy (CTEM) of the fracture surface of specimens subjected to four-point bending. The composites studied in this work were produced by directional solidification, which gives an in-situ composite microstructure consisting of Nb_3Si type dendrites surrounded by a eutectic of a niobium solid solution and a niobium silicide. Using CTEM it is possible to view directly the micromechanisms of fracture, including the details of slip transmission between phases, microcracking, crack bridging, ductile-phase pull-out, and interfacial debonding. Using CTEM it has been possible to observe significant differences in the fracture behavior of these composite materials, and to correlate these observations with the mechanical properties.

11:00 AM

PHASE STABILITY AND HARDNESS OF Mo-SILICIDE ALLOYS WITH ADDITIONS OF Ni, Al, AND B: *J. W. Cohron*[1]; E. P. George[1]; [1]Oak Ridge National Laboratory, Metals and Ceramics Division, P.O. Box 2008, Oak Ridge, TN 37831 USA

A preliminary investigation of phase stability and hardness changes as a function of Ni, Al and/or B in Mo-silicides has been performed. Phases and their relative amounts were obtained using X-ray diffraction (XRD). Hardness measurements were made on each alloy. The propensity for crack formation, coupled with the measured hardness numbers, gave an indication of the relative toughness of each alloy. In the absence of B and with increasing additions of Al and Ni, hardness and cracking decreased. Presumably, this "softening" is due to the increasing formation of the NiAl phase, which is evident in the XRD patterns. With the addition of B, hardness and crack formation increased. This decrease in toughness has been associated with the formation of a brittle $Mo_5(Si,B)_3$ phase, again, as indicated by the XRD data. Primary and secondary phases and their relative stability are discussed as a function of alloy composition. Research sponsored by the Division of Materials Sciences, U.S. Department of Energy under contract DE-AC05-96OR22464 with Lockheed Martin Energy Research Corp.

11:20 AM
SYNTHESIS AND PROPERTIES OF IN-SITU (Mo,W)Si_2 COMPOSITES: *Dae Kyu Jang*[1]; Reza Abbaschian[1]; [1]Korea Institute of Geology, Mining and Mats., Resources Utilization & Mats. Division, 30, Kajung-Dong, Yusung-ku, Taejon 305-390 Korea

(Mo,W)Si_2 composites were prepared by vacuum hot pressing from elemental Mo, W and Si powders at various temperatures. The Microstructure and properties of these materials were characterised by using X-ray diffraction, scanning electron microscopy, energy dispersive x-ray spectroscopy and Vicker's technique. The synthesis of in-situ (Mo,W)Si_2 composites did not show the presence of any unreacted elements. Microstructural and x-ray analysis showed that (Mo.W)Si_2 alloys formed. The grain size of the (Mo,W)Si_2 was relatively uniform. The grain size of the (Mo.W)Si_2 composites is smaller than that in monolithic $MoSi_2$. The room temperature hardnesses of the composites increase with increasing reaction temperature.

11:40 AM
STRENGTH AND FRACTURE TOUGHNESS OF CAST Mo-12Si-8.5B (AT. %) INTERMETALLICS: *Joachim H. Schneibel*[1]; C. T. Liu[1]; Cecil A. Carmichael[1]; [1]Oak Ridge National Laboratory, Metals and Ceramics Division, P.O. Box 2008, Oak Ridge, TN 37831-6115 USA

Alloys with the composition Mo-12Si-8.5B (at. %) were prepared by arc-melting. They contained approximately 40 vol.% of α-Mo inclusions in a brittle matrix of 30 vol.% Mo3Si and 30 vol.% Mo_5SiB_2 (T2). The room temperature flexure strength and fracture toughness of the as-cast alloys were 450 MPa and 7 MPa $m^{1/2}$, respectively. A heat treatment of 1 day at 1873 K in vacuum increased the room temperature fracture toughness to 10 MPa $m^{1/2}$. Consistent with ductile phase toughening, the fracture surfaces revealed plastic deformation as well as debonding of the α-Mo. Testing at 773 K resulted in flexure strengths as high as 700 MPa. All these experiments suggest that the mechanical properties of the α-Mo solid solution are critical in determining the mechanical properties of these Mo-Si-B alloys. This research was sponsored by the Fossil Energy Advanced Research and Technology Development (AR&TD) Materials Program, U.S. Department of Energy, under contract DE-AC05-96OR22464 with Lockheed Martin Energy Research Corporation.

SURFACE ENGINEERING: SCIENCE AND TECHNOLOGY I: Nanostructured Materials

Sponsored by: Materials Processing and Manufacturing Division, Surface Engineering Committee
Program Organizers: Yip-Wah Chung, Northwestern University, Dept. of Mats. Sci & Eng., Evanston, IL 60208 USA; Ashok Kumar, University of South Alabama, Dept. of Elect. & Comp Eng., Mobile, AL 36688-0022 USA; John E. Smugeresky, Sandia National Labs, Livermore, CA 94551-0969 USA

Tuesday AM Room: 7B
March 2, 1999 Location: Convention Center

Session Chairs: Delcie R. Durham, National Science Foundation, 4201 Wilson Blvd., Arlington, VA 22230 USA; F. Huisken, Max-Planck-Institut für Stromungsforschung, Brunsenstr 10 D-37073, Göttingen Germany

8:30 AM INVITED PAPER
NANOSTRUCTURED COATINGS: *J. M. Aikens*[1]; H. Sarkas[1]; R. W. Brotzman[1]; [1]Nanophase Technologies Corporation, 453 Commerce St., Burr Ridge, IL 60521 USA

The development of nanostructured coatings with improved abrasion resistance, EM shielding, thermal conductivity, refractive index, and transparency requires careful manipulation of material composition, nano-structure size, and composite structure. The selected materials must be processable and yield the desired physical properties. The correct nanostructure size is important because often multiple physical properties are desired, i.e., conductivity or abrasion resistance with transparency. The correct composite structure must be selected for the desired physical property from uniform surface distribution for abrasion resistance to connected structures for electrical conductivity. Nanostructured coatings formed by the addition of dense, crystalline nanoparticles to a continuous second phase will be discussed. The particles are manufactured by gas phase condensation and the continuous phase varies from epoxy polymers to silica. Particle size, material composition, and surface treatments are manipulated to control composite properties and structure. Transparent/conductive, transparent/abrasion resistant, and transparent/high refractive index coatings will be discussed with respect to a broad range of market applications including electronic materials, optical and magnetic devices, catalysts, and structural materials.

8:55 AM
THIN LIQUID FILM ELECTRO SPRAYING- A NOVEL COATING TECHNOLOGY: *Gunnar Sorensen,* Institute of Physics and Astronomy, Aarhus University, 8000 DK Aarhus C, Denmark

A novel coating technology has been developed for suspensions and solutions in a dielectric medium. A thin liquid film of this medium is flowing to a spraying nozzle at a high voltage of 2-20 kV. A glass cylinder acts as an electrostatic lens surrounding the spraying system which in a simple version can be a modified hypodermic syringe needle. Ultrafine powder down to 0.2 micron can be collected on a grounded substrate. Various spraying nozzæes will be discussed, and examples of depositing ultrafine powders on surfaces will be presented. Examples comprise deposition of nano-diamond powder, carbon 60 and the biomolecule azoadenine for sputtering C-N compounds

9:10 AM INVITED PAPER
LASER-INDUCED PRODUCTION AND CHARACTERIZATION OF CRYSTALLINE SILICON NANOPARTICLES WITH NARROW SIZE DISTRIBUTION: *F. Huisken,* M. Ehbrecht, and B. Kohn, Max-Planck-Institut für Strömungsforschung, Bunsenstr. 10, D-37073 Göttingen, Germany

Silicon clusters and nanoparticles are produced by CO_2-laser-induced gas phase reactions in a flow reactor. In contrast to conventional techniques, the particles are expanded, directly after production, through a conical nozzle into a high vacuum chamber and then transferred into a molecular beam machine where they are analyzed in situ with a time-of-flight mass spectrometer. The analysis reveals that the flow reactor emits, besides small silicon clusters, also high-purity silicon crystallites with diameters between 1 and 10 nm. It is found that the particles* velocity strongly correlates with their mass. This feature and the fact that the particles are produced in a pulsed mode (by using a pulsed CO_2 laser) enable us, by introducing a chopper into the cluster beam, to considerably reduce the dispersion of their size distribution and to perform size-selected low-energy cluster deposition on various substrates. High resolution transmission micrographs demonstrate the capabilities of the new apparatus. The monodispersed silicon films have been further characterized by studying their luminescence and Raman scattering behavior. As predicted by theoretical models, the peak of the luminescence curve shifts with decreasing particle size to smaller wavelengths (higher energies). In addition, it is found that the efficiency curve has a sharp maximum for particles with 4 nm diameter.

9:35 AM INVITED PAPER
RECENT DEVELOPMENT IN LASER-ASSISTED CHEMICAL VAPOR DEPOSITION OF NANOPOWDERS AND COATINGS: *Rodica Alexandrescu*[1]; [1]National Institute for Laser, Plasma and Radiation Physics, P.O. Box MG-36, Bucharest Romania

Laser-assisted chemical vapor deposition (CVD) method plays an important role in producing solid-state materials because of its potentialities to be applied to a wide variety of compounds (nitrides, carbides and metal-based products) together with its ability to control the chemical and physical properties of the new produced material. Although related by similar experimental technique, the differences between thin film deposition and the powder synthesis by laser CVD rely in the

magnitude of the growth time (or residence time in the laser beam) and in the density of nucleated particles. Fast heating and cooling processes and high particles densities are characterized nanophase powder synthesis. In this paper the synthesis of iron-based and carbon nitride napophase powders and thin films are discussed, in order to demonstrate the multiple possibilities provided by laser assisted CVD processing for the production of materials with tailored properties. For iron-based deposition, the gas-phase decomposition of iron pentacarbonyl is an area of current interest. Iron carbides fine powders were obtained by the CO2 laser pyrolysis of sensitized (SF6) mixtures and different carrier gases (C2H4, C2H2) for Fe(CO)5 vapors: non-aggregated particles with mean size in the range 6 nm were obtained for acetylene/iron pentacarbonyl mixtures. As concerning iron-based film deposition, a comparative analysis of coatings obtained by photolytic and thermal laser-induced processes indicate that specific growth mechanism influence the film structure and chemical composition. The carbon nitride thin film and nano powders were synthesized from hydrocarbon/ammonia mixtures. The CNx thin films were obtained at two irradiation wavelengths on different substrates. The CN powders were produced by the IR pyrolysis of acetylene/ammonia/nitrous oxide mixtures. The different chemical and crystallographic phases of the obtained materials are discussed.

10:00 AM INVITED PAPER

AN INVESTIGATION OF THE RELATIONSHIP BETWEEN STRUCTURE, SURFACE ROUGHNESS AND HARDNESS BY TiN THIN FILMS DEPOSITED BY RF SPUTTERED PVD PROCESS: *Delcie R. Durham*[1]; Carl Carney[1]; [1]National Science Foundation, 4201 Wilson Blvd., Room 530, Arlington, VA 22230 USA

The growth of a thin film on a substrate is dependent upon the process, the substrate preparation and any additional “drivers” to the system. An ECR plasma enhanced reactive sputtering technique was used to deposit the TiN films of 1 - 2 micrometers thickness on Inconel 718 polished substrates. The PVD process is enhanced using Electron Cyclotron Resonance (ECR) which allows broader options in selecting the basic processing conditions. The properties of the TiN thin films have been shown to be dependent upon the temperature of the substrate, substrate bias, flow conditions within the plasma and the pressure in the chamber. For example, lower deposition temperatures are desirable to reduce substrate microstructural changes and to reduce the thermal stresses developed in the films. Typically, lower pressures are also advantageous, since they provide for longer mean free path movement of the species being deposited. A 24 designed experiment was conducted to investigate the individual and combined effects of substrate temperature, substrate bias, system pressure and nitrogen flow. An additional investigation included the effects of microwave power. The films obtained were polycrystalline, with varying crystallographic structures, grain size, and surface roughness, and hardness. After deposition, the films were characterized using the x-ray diffractometer, the SEM and the AFM, a Digital Instruments nano-indentor as well as microhardness tests and standard profilometry. Characterization of the film surface was accomplished by standard profilometry and by atomic force microscopy (AFM) techniques. RMS roughness and fractal roughness information was obtained for the films produced. The fractal dimension for the film surface was determined by AFM methods, providing data at the nanoscale level. The fractal dimension can provide significantly more detail regarding fine variations in the surface topography than RMS information can provide. When the RMS roughness and the fractal number data were compared for the set of tests, there is no clear correlation between these two methods of describing surface roughness. There appears to be a stronger relationship between fractal roughness and hardness than between RMS roughness and hardness. The relationship with crystal orientation is not strong, although when [200] growth was suppressed, nanohardness of over 30 micrometers was obtained. Those films which exhibited fine, or very fine columnar grains had the higher hardness as expected.

10:25 AM BREAK

10:40 AM INVITED PAPER

DESIGN OF NANOSTRUCTURED THIN FILMS FOR TRIBOLOGICAL APPLICATIONS: *H. Holleck*[1]; [1]Institut fur Material-und Festkorperforschung 1, Kemforschungszentrum Karlsruhe, Postfach 3640, Karlsruhe 1 W-7500 Germany

Nanoscaled coatings for tribological applications can be subdivided into nanostructured multilayer films, nanomodulated superlattice films, nanocrystalline films, nanostabilized single and multilayer films and nanograded films. Aside from materials selection and deposition characteristics, the interface volume, grain size, single layer thickness, surface and interface energy, texture and the epitaxial stress and strain are principal factors determining constitution, properties and performance of these coatings. The functional and structural design of multilayer coatings can result in tailored multifunctional coatings as it is shown for nanoscaled TiN/TiAlN, TiC/TiB2 , TiN/MoS2 and TiC/C multilayer films. The influence of the modulation of composition, structure, stress and strain in so called superlattice films on the properties is discussed in dependence on the modulation period and the material selection. Nanocrystalline coatings (e.g. TiC/TiB2 , TiC/C or TiN/MoS2 films) are well suited to combine film materials with similar or extremely different bonding characteristics to a multifunctional composite coating. New structures for thin film materials or specific film textures can be stabilized by epitaxial growth in nanostabilized multilayer coatings. The stabilization of fcc AlN, fcc SiC, crystalline C3N4 and wurtzite type BN are examples for materials which operate successfully or are in the state of development. New metastable nanocrystalline films can be deposited by vapor quenching. A thermodynamic and kinetic modeling results in new film materials (e.g.TiBCN), tailored with respect to constitution, properties and performance.

11:05 AM

DIAMOND-LIKE NANOCOMPOSITE COATINGS FOR SPACE APPLICATIONS: *Craig A. Outten*[1]; Daniel Kester[1]; Chandra Venkatraman[1]; Donald Bray[1]; Chris Halter[1]; [1]Advanced Refractory Technologies, 699 Hertel Ave., Buffalo, NY 14207 USA

In recent studies, Diamond-Like Nanocomposite (DYLYN®) coatings were found to possess resistance to atomic oxygen, tailorable electrical conductivity, and excellent mechanical properties. Therefore, several potential applications are anticipated on critical optical, electronic, thermal, and mechanical components for commercial and military Low Earth Orbit spacecraft systems. The coatings were deposited with a proprietary plasma-assisted chemical vapor deposited process. In particular, electrically conductive coatings (as low as 1800 ohms per square) were deposited on flexible plastic substrates, e.g. Kapton® and Mylar®. The coated substrates were subjected to ground based atomic oxygen testing. The results indicated that DYLYN® coatings reduced erosion yields on Kapton® and Mylar® by 130X and 50X, respectively. Furthermore, the coatings on plastics exhibit high flexibility and were bent to a radii less than 1/32" with no damage to the coating. Further mechanical testing is presented to demonstrate the coating’s durability. A brief discussion is included of the DYLYN® coatings which were flown on the NASA Optical Properties Monitor (OPM) Experiment.

11:20 AM INVITED PAPER

NANOSCALE CONTROLLED GROWTH, PROPERTIES, AND NOVEL DEVICE APPLICATIONS OF EPITAXIAL THIN FILMS OF CONDUCTIVE MAGNETIC OXIDE SrRuO3: *Chang-Beom Eom*[1]; [1]Duke University, Dept. of Mech. Eng. and Mats. Sci., Durham, NC 27708 USA

Oxide materials possess an enormous range of electrical, optical, and magnetic properties. For instance, insulators, high quality metals, dielectrics, ferroelectrics, piezoelectrics, semiconductors, ferromagnetics, transparent conductors, colossal magnetoresistance materials, superconductors, and nonlinear optic materials have all been produced using oxide materials. Therefore, thin films and heterostructures of oxide materials have great potential for novel device applications. For many of these device applications, it is necessary to have epitaxial growth of conductive oxide thin films in a single heterostructure. We have grown epitaxial thin films and heterostrcutures of conductive magnetic oxides, SrRuO3(1) in situ by 90Ῠ off-axis sputtering and pulse laser deposition. SrRuO3 is a distorted perovskite with a GdFeO3-type structure and undergoes a ferromagnetic transition at 160K. Single crystal epitaxial SrRuO3 thin films were obtained on vicinal (001) SrTiO3 substrates with a large miscut angle and miscut direction close to the [010] axis. Scanning tunneling microscopy revealed that the growth mechanism changed

from two dimensional nucleation to step flow growth as the miscut angle increased(2). The electrical transport, magnetoresistance and novel ferroelectric(3) and magnetic device applications of the conductive ferromagnetic oxide thin films and heterostructures will be discussed. (1) C. B. Eom et al., Science, 258, 1766 (1992); (2) R.A. Rao, Q. Gan, and C.B. Eom, Appl. Phys. Letts. 71, 1171 (1997); (3) C. B. Eom et al., Appl. Phys. Letts., 63, 2570 (1993). This work was supported by the ONR Grant No. N00014-95-1-0513, NSF Grant No. DMR 980244, the NSF Young Investigator Award (CBE) and the David and Lucile Packard Fellowship (CBE).

11:45 PM

MECHANICAL AND TRIBOLOGICAL PROPERTIES OF NANOSTRUCTURED DIAMOND FILMS ON Ti-6Al-4V SUBSTRATES: *Shane A. Catledge*[1]; Yogesh K. Vohra[1]; [1]University of Alabama at Birmingham, Dept. of Physics, Birmingham, AL 35294-1170 USA

Microwave plasma chemical vapor deposition (MPCVD) was used to deposit diamond films onto Ti-6Al-4V substrates at high density plasma processing conditions which can be tailored to result in a range of microstructures ranging from crystalline to nano-crystalline diamond. Micro-Raman spectroscopy, glancing-angle x-ray diffraction (XRD) and scanning electron microscopy (SEM) were used to characterize the structure of the films. The average surface roughness of the nano-crystalline films as measured by profilometry was 40 nm and the average hardness/ elastic modulus of the films as measured by nano-indentation was 90 GPa/ 700 GPa. The adhesion of the films produced by our high density plasma processing technique is significantly better than films produced by conventional processing conditions as qualitatively observed by the lack of spallation for substrate temperatures up to 850 ?C. Further quantitative adhesion and wear-resistance tests were performed on the diamond films. The improved adhesion, low surface roughness, and high hardness of these diamond films make them attractive for a variety of tribological applications.

12:00 PM

NANOSCALE MECHANICAL, FRICTION, AND WEAR PROPERTIES OF MATERIALS FOR MEMS APPLICATIONS: *Oden L. Warren*[1]; L. L. Kuhn[1]; D. A. Crowson[1]; T. Wyrobek[1]; [1]Hysitron, Inc., 5251 West 73rd St., Minneapolis, MN USA

The primary goal of many emerging device technologies, such as microelectromechanical systems (MEMS), is to achieve macroscale functionality from microscale components. Further miniaturization of these device technologies will result in progressively smaller clearances between moving parts, which will inevitably increase the occurrence of tribological contacts between surfaces. Because MEMS devices often lack sufficient reserve power to shear adhesive junctions, even the first contact event can lead to irreversible formation of an interface. Therefore, optimization of device design parameters will eventually require knowledge of mechanical, friction, and wear properties of surfaces down to the atomic scale. Quantification of these properties down to the nanoscale is now achievable due to recent improvements in depth-sensing nanoindentation instrumentation. Here, we discuss new developments in lateral displacement actuation and lateral force measurement with a capacitance-based nanoindenter. Coupling this novel self-contained technology to a scanning probe microscope results in unprecedented utility for tribological and mechanical properties investigations at the nanoscale. Results of case studies relating to materials for MEMS applications will also be presented.

12:15 PM

SYNTHESIS OF THIN FILMS OF SILICON NANOPARTICLES WITH SIZE CONTROLLED BY REACTION PARAMETERS: *S. Botti*[1]; R. Coppola[1]; E. Massetti[1]; [1]ENEA, Dipartimento Innovazione, Divisione Fisica Applicata, Centro Ricerche Frascati, Rome Italy

Nanoscale silicon is attracting considerable interest due to its electronic quantum-size effect. The CO2 laser induced pyrolisis of gas phase reactants has proved to be a viable tool for producing ultrafine particles and has been applied to the synthesis of nanosized silicon particles. The powders synthesis occurs by heating the reactant gases up to the dissociation limit with a 500 W CO2 laser. The reactants interact in a laminar flow confined by a carrier beam (He, Ar) in a collision environment. For the silicon synthesis the silane provides the coupling with laser radiation due its strong absorption at 10.6 ?m. The silicon particle growth is controlled by on-line optical technique and the silicon particle diameter has been scaled in a wide size range (2-100 nm). By this technique it is possible also to fabricate thin film comprised of size selected nanoparticles. By a secondary nozzle the reaction products are extracted at right angle to both the gas flow and laser beam and are expanded in a differential chamber before the deposition on heated substrate. Photoluminescence properties of thin film and powders synthesized

SYNTHESIS OF LIGHTWEIGHT METALS III: Semi-Solid Processing

Sponsored by: Light Metals Division, Aluminum Committee; Structural Materials Division, Titanium Committee; ASM International: Materials Science Critical Technology Sector, Materials Synthesis & Processing Committee

Program Organizers: F. H. (Sam) Froes, University of Idaho, IMAP-Mines Bldg. #321, Moscow, ID 83844-3026 USA; C.M. Ward Close, DERA Farnborough, Structural Mats. Ctr, Farnborough, Hampshire GUI14OLX UK; D. Eliezer, Ben Gurion University, Dept. of Mats. Eng., Neqev Israel; P. G. McCormick, University of W. Australia, Res. Ctr for Adv. Min. & Mat. Proc., Nedlands, W.A. 6907 Australia

Tuesday AM Room: 10
March 2, 1999 Location: Convention Center

Session Chairs: Robert Dax, Concurrent Technologies Corporation, Johnstown, PA 15904 USA; Helen Atkinson, The University of Sheffield, Dept. of Eng. Mats., Sheffield, South Yorkshire S1 3JD UK

8:30 AM INVITED PAPER

EFFECT OF SEMI SOLID PROCESSING ON THE MICROSTRUCTURE AND MECHANICAL PROPERTIES OF ALUMINUM MATRIX COMPOSITES - PART I: *F. Robert Dax*[1]; Tim Freidhoff[1]; Juan J. Valencia[1]; [1]Concurrent Technologies Corporation, 1450 Scalp Ave., Johnstown, PA 15904 USA

Metal matrix composites (MMC) have not been used as extensively as forecast for a variety of reasons. One is the extreme difficulty of machining and grinding MMCs because of the hard second phase. Semi solid metalworking (SSM) offers the potential to form these materials into very complex parts (net shape) while maintaining a homogeneous distribution of the hard second phase within the part. This paper will provide an overview of SSM processing of various aluminum matrix composites, including aluminum A357 + SiC, 6092 + SiC, A356 + SiB6, and in situ Al+25%Si+4%Cu. In addition, the effect of SSM on microstructure and mechanical properties and will also be presented. This work was conducted by the National Center for Excellence in Metalworking Technology operated by Concurrent Technologies Corporation under contract No. N00140-92-C-BC49 to the U.S. Navy as part of the U.S. Navy Manufacturing Technology Program.

8:50 AM INVITED PAPER

EFFECT OF SEMI SOLID PROCESSING ON THE MICROSTRUCTURE AND MECHANICAL PROPERTIES OF ALUMINUM MATRIX COMPOSITES - PART II: *F. Robert Dax*[1]; Tim Freidhoff[1]; Juan J. Valencia[1]; [1]Concurrent Technologies Corporation, 1450 Scalp Ave., Johnstown, PA 15904 USA

9:10 AM

ADVANCES IN THIXOMOLDING: *D. Matthew Walukas*[1]; Raymond F. Decker[1]; Stephen E. LeBeau[1]; [1]Thixomat, Inc., 717 E. Huron St., Ann Arbor, MI 48104 USA

Thixomolding® is a one step that produces net-shape parts through high speed injection molding of semi-solid thixotropic alloys. A de-

scription of the process will be presented. Microstructural effects and reduced porosity result in improved properties of magnesium alloys. Mechanical properties and microstructures of Thixomolded® AZ91D will be presented. Data on enhanced creep and corrosion properties of Thixomolded® AZ91D will be compared to die AZ91D. Preliminary developments in aluminum Thixomolding® will be covered.

9:30 AM
SOME CRITERIA FOR MATERIAL SELECTION FOR SEMISOLID PROCESSING: *Antonios Zavaliangos*[1]; Evangelos Tzimas[1]; [1]Drexel University, Dept. of Mats. Eng., 32 and Chesnut St., Philadelphia, PA 19104 USA

The important microstructural parameters that determine whether a material is suitable for thixoforming are (i) adequate volume fraction of solid, (ii) equiaxed morphology of the solid grains, and (iii) minimum entrapped liquid. In this paper we introduce a simple criterion for processability in the semisolid range based on the sensitivity of the volume fraction of solid with respect to minor temperature variations. In addition we propose that the processability in the semisolid state can be enhanced using microsegregated material.

9:50 AM BREAK

10:05 AM
EXPERIMENTAL DETERMINATION OF PARAMETERS REQUIRED FOR MODELLING OF SEMI-SOLID PROCESSING: *Helen Valerie Atkinson*[1]; [1]The University of Sheffield, Dept. of Eng. Mats., Sir Robert Hadfield Bldg., Mappin St., Sheffield, South Yorkshire S1 3JD UK

Numerical modelling of the filling of dies in semi-solid processing could help to ensure defect-free products and to avoid costly and time-consuming trial and error with die design and process variables. All numerical models require the input of experimental data on material parameters. These data can be obtained from rheological investigations in rheometers. However, semi-solid processing is generally carried out with fractions of solid above 0.5 and rheometers can only function with fractions of solid below about 0.4. Alternatively, rapid compression experiments can be used with high fractions solid but these have inherent drawbacks. This paper will review the various approaches to obtaining data on material properties as required for numerical modelling.

10:25 AM
EFFECT OF ULTRASONIC TREATMENT ON SUBSEQUENT SEMI-SOLID PROCESSING: *Nico DeSmedt*[1]; B. Bishoff[2]; R. Wagstaff[2]; O. N. Senkov[1]; F.H. (Sam) Froes[1]; [1]University of Idaho, IMAP, Mines Bldg., Rm. 321, Moscow , ID 83844-3026 USA; [2]Wagstaff Engineering, N. 3910 Flora Rd., Spokane, WA 99216 USA

Use of ultrasonic treatment can lead to a grain refinement and reduction in secondary dendrite arm spacing (SDAS) in direct chill (DC) aluminum billets. In this paper the effect of a number of parameters including alloy type, grain refiners, billet size and positioning of the ultrasonic transducer on the grain size and SDAS will be discussed. Consideration will also be given to the behavior of ultrasonically treated billets on subsequent semi-solid processing.

10:45 AM
HIGH TEMPERATURE CREEP RESPONSE OF THE AZ91 MAGNESIUM ALLOY PRODUCED BY THIXOFORMING: E. Evangelista[1]; M. Cabibbo[1]; S. Spigarelli[1]; A. Rosen[2]; University of Ancona, [1]INFM/Department of Mechanics, Ancona, Italy 60131; [2]Technion, Dept. of Materials Engineering, Haifa, Israel 32000

The creep response of an AZ91 alloy produced by thixoforming was investigated at 120, 135 and 185°C. The microstructure of the alloy after thixoforming consisted in a distribution of a globules separated by a divorced eutectic composed by small a particles surrounded by b brittle phase. The creep curves exhibited a short primary region, followed by a minimum creep rate range and an extended tertiary stage; the maximum rupture elongation approached 20%. The minimum creep rate dependence on applied stress showed a reduction of the m parameter ($m=\P\log e_m/\P\log s)_{T=cost}$ with stress, suggesting a variation of the creep controlling mechanism. The activation energy for creep ($Q=\P\ln e_m/\P(1/T))_{s=cost.}$ was 111 and 145 kJ/mol at 80 and 100 MPa respectively. Both the minimum creep rate dependence on applied stress and the reduction of activation energy for creep with stress were in close analogy with the creep response of die cast AZ91 having similar microstructure; this result and the presence of a distribution of fine a grains, in turn, support the idea that in the low stress region grain boundary sliding could become rate controlling.

THE MARTIN E. GLICKSMAN SYMPOSIUM ON SOLIDIFICATION AND CRYSTAL GROWTH: Solidification: Modeling

Sponsored by: Materials Processing and Manufacturing Division, Solidification Committee

Program Organizers: Dr. N. B. Singh, Northrop Grumman Corporation, Pittsburgh, PA 15235 USA; Dr. Steven P. Marsh, Naval Research Laboratory, Code 6325, Washington, D.C. 20375 USA; Krishna Rajan, Rensselaer Polytechnic Inst., Dept. of Mats. Sci & Eng., Troy, NY 12180-3590 USA; Prof. Peter W. Voorhees, Northwestern University, Dept. of Mats. Sci. & Eng., Evanston, IL 60208 USA

Tuesday AM — Room: 11A
March 2, 1999 — Location: Convention Center

Session Chairs: Sam R. Coriell, NIST, Dept. of Metall., Gaithersburg, MD 20899 USA; Ranga Narayanan, University of Florida, Dept. of Chem. Eng., Gainesville, FL USA; Reza Abbaschian, University of Florida, Dept. of Mats. Sci. and Eng., Gainesville, FL 32611 USA

8:30 AM INTRODUCTION

8:45 AM
SEGREGATION SUBSTRUCTURES IN DILUTE Al-Cu ALLOYS DIRECTIONALLY SOLIDIFIED: *O. Fornaro*[1]; H. Palacio[1]; H. Biloni[2]; [1]IFIMAT-CIC-UNICEN, Tandil Argentina; [2]LEMIT-CIC, La Plata Argentina

At low and moderate solidification velocities, the decrease of the parameter GL/VCo (GL: Thermal gradient in the liquid in front of the Solid-Liquid interface, V: S-L interface velocity, Co Alloy composition) controls the evolution of the S-L interface from plane to dendritic. Even the evolution of the instabilities is continuous, with the increase of the constitutional supercooling (CS) the following stages, in f.c.c. alloys, may be defined: (i) planar interface; (ii) nodes or depressions of the S-L interface; (iii) elongated or bidimensional cells; (iv) regular hexagonal cells; (v) distorted or branched cells and (iv) dendritic cells. Extensive research, both experimental and theoretical has been done by several authors on the evolution of the S-L interface, both in dilute alloys and organic transparent alloys, using the linear stability theory where the CS is a particular case. Considering that after the passage of the solidification front, a variation of composition remains on a length scale characteristic of the cellular or dendritic growth, that is called microsegregation, we stress that a careful and suitable metallographic analysis can give good information in 3D symmetry on the mechanisms involved in the evolution of the segregation substructure, where still the transition between cellular and dendritic substructures at low and intermediate velocities are not well understood. Under this frame, unidirectional growth of dilute Al-Cu alloys between 0.2 and 0.5 wt. % Cu, were performed under controlled conditions of the GL and V using a quenching technique of the S-L interface. The metallographic analysis of the segregation patterns behind the frozen interface in longitudinal and transverse sections gives information about the effect of the local solidification conditions, which results in small wall instabilities during the lateral growth of the cells. These instabilities seems to control the formation or disappearance of cellular walls, a mechanism necessary for the evolution of the substructure through the different stages above

mentioned. At the same time a more complete microsegregation map associated with the bulk crystalline growth of the alloys has been obtained.

9:15 AM
EVOLUTION EFFECTS IN DENDRITIC SOLIDIFICATION: *Arnon Chait*[1]; Vladimir Pines[2]; Marianne Zlaatkowski[2]; Matthew Koss[2]; Martin Glicksman[2]; [1]NASA Lewis Research Center, Brook Park Rd., Cleveland, OH 44135 USA; [2]R. P. I., Dept. of Mats. Sci. and Eng., Troy, NY 12180 USA

We examine evolution effects predicted from the recently developed two-parameter scaling theory in dendritic growth (Pines, Chait, Zlatkowski). For sufficiently small levels of supercooling, it was demonstrated that an additional scaling parameter is necessary to completely solve the dendrite selection problem. The new parameter was shown to be related to the initial characteristic nucleus size. We propose a novel microgravity experiment (Transient Dendritic Solidification Experiment) to study dynamic events in dendritic growth. Using rapid pressurization/depressurization we can obtain fast changes in the effective supercooling via the Clapeyron effect on the melting temperature. A hypothetical cycle of increasing/decreasing pressure is examined using a fully numerical nonlinear simulation. We explore the potential role of the initial nucleus size via a direct inspection of hysteresis effects in the dendrite operating state (tip radius and velocity) at the same supercooling level originating from different initial conditions.

9:35 AM INVITED PAPER
FLOW-INDUCED MORPHOLOGIES: *Stephen Davis*[1]; [1]Northwestern University, Evanston, IL 60208 USA

Consider the directional solidification of a dilute binary alloy. The front can be unstable to cellular structures in the absence of melt flow. When the melt undergoes fluid flow, the rejected solute can be redistributed so as to create new morphologies. In the presentation, examples will be discussed of hydrodynamic instabilities interacting with solid-melt interfaces (Benard convection, Taylor-Couette flow), forced flows on propagating interfaces, and some recent results on convective flows.

9:55 AM INVITED PAPER
DENDRITIC GROWTH-DEVIATIONS FORM THE IDEAL: *Robert J. Schaefer*[1]; R. E. Napolitano[1]; [1]NIST, Dept. of Metall., Gaithersburg, MD 20899 USA

Much of our understanding of dendritic growth comes from studies under well-controlled laboratory conditions: in isothermal, supercooled liquids or in constant gradients moving at constant velocity. However, when single crystal superalloy components are produced for use in aircraft engines, the dendrites encounter more complex, transient thermal environments which may lead to defective structures. A predictive model for the development of such defects needs to include several components, including a model describing the thermal field, a model describing the kinetics of growth of the dendrite and its branches, and a model describing how defect formation depends on the local thermal conditions. Here we describe how some of these components can be constructed and put together to estimate the tendency for defect formation. The most difficult part of the model to quantify is the description of the relation between thermal conditions and defect formation.

10:15 AM BREAK

10:35 AM INVITED PAPER
FORMATION OF SUPERSATURATED SEMICONDUCTOR ALLOYS: *J. Narayan*[1]; [1]North Carolina State University, Dept. of Mats. Sci. and Eng., Raleigh, NC 27695 USA

By controlling interface velocity during crystallization in liquid-phase, it is possible to far exceed equilibrium solid solubility limits in silicon via solute trapping. There is an interesting parallel in solid-phase crystallization, where by controlling the interface morphology and velocity, it is possible to achieve equally high solubility limits (supersaturation) as much as a factor of 500 or more. The emphasis in this talk will be placed on interface kinetics and instability and their correlation with formation of defects such as twins during crystallization. The impact of these fundamental studies on the formation of defect-free shallow junctions and ohmic contacts are discussed in the context of next-generation semiconductor devices.

11:05 AM
INCREMENTAL CRYSTAL GROWTH IN DROPLET DEPOSITION: *Teiichi Ando*[1]; Charles D. Tuffile[1]; [1]Northeastern University, Dept. of Mech., Industr. and Manufact. Eng., 334 Snell Eng. Center, Boston, MA 02115 USA

Molten uniform droplets of Sn - Pb alloys having the same diameter were generated by the controlled breakup of a laminar jet and deposited onto a temperature- and motion-controlled substrate at different droplet temperatures and liquid fractions. Spray deposits so produced presented different microstructures ranging from fine, equiaxed microstructures, to those of columnar or single crystals. The columnar or single-crystalline growth in spray deposition with uniform-droplets differs from conventional columnar or single-crystalline growth in that the crystals are grown incrementally by the rapid epitaxial solidification of the depositing droplets. The resultant crystals thus present features of a rapid solidification microstructure. Such modes of crystal growth are only possible with fully molten droplets deposited under controlled conditions. Spray and substrate conditions required for the different novel microstructures are discussed.

11:35 AM
DENDRITE MORPHOLOGY DURING DIRECTIONAL SOLIDIFICATION OF BINARY ALLOYS: *Y. Lu*[1]; S. N. Ojha[2]; J. Reye[1]; G. Ding[1]; *S. N. Tewari*[1]; [1]Cleveland State University, Dept. of Chem. Eng., Cleveland, OH 44135 USA; [2]B.H.U.,Dept. of Metall., Varanasi, UP India

Theoretical models of dendritic arrayed growth assume a steady-state dendrite morphology and predict dendrite tip radius, tip composition, tip temperature and primary dendrite spacing as a function of growth parameters (alloy composition, thermal gradient and growth speed) and alloy physical properties. Directional solidification of binary metallic alloys followed by a rapid quench to retain the mushy zone morphology is the only technique which would allow a simultaneous measurement of all these features in order to carry out a meaningful evaluation of these models. Since the metallic alloys are opaque serial sectioning of dendrites in the quenched mushy zone followed by a superimposition of metallographic images is required to visualize the three dimensional dendritic morphology. Results will be presented from our experiments on Pb- 5.8 wt pct Sb alloy. The experiments indicate that the dendrite tips are not axisymmetric, their tip morphology is determined by their immediate neighbors and they do not have a steady-state tip shape, i.e., the tip morphology does not remain constant, it fluctuates within a shape envelope. The cellular arrays show more extensive tip shape fluctuation as compared with the dendrites. It, however, is not certain whether these effects are due to the natural competition among neighboring dendrites or an artifact due to convection in the melt which is ever present during terrestrial directional solidification experiments. This research was supported by NASA- Microgravity Science and Applications Division.

EPD Luncheon
Time: 12:00 Noon
Room: Marina Ballroom
Location: Marriott Hotel

Tutorial Luncheon Lecture: "Dynamic Behavior of Materials"
Time: 12:00 Noon - 1:30 PM
Room: 16A
Location: San Diego Convention Center

EPD Distinguished Lecturer
Time: 1:45 PM
Room: Marina Ballroom
Location: Marriott Hotel

11TH INTERNATIONAL SYMPOSIUM ON EXPERIMENTAL METHODS FOR MICROGRAVITY MATERIALS SCIENCE: Session III

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

Program Organizer: R. A. Schiffman, R.S. Research, Inc., Crystal Lake, Barton, VT 05822 USA; C. Patuelli, Dipartimento di Fisica and Istituto Nazionale ci Fisica per la Materia, Alma Mater Studiorum, Berti Pichat 6/2, 40127 Bologna, Italy

Tuesday PM Room: 15B
March 2, 1999 Location: Convention Center

Session Chair: J. B. Andrews, University of Alabama at Birmingham, Dept. of Mats. and Mech. Eng., Birmingham, AL 35294 USA

2:00 PM

AN EXPERIMENTAL STUDY OF THE DYNAMICS OF A HEATED DOMAIN IN SUPERCRITICAL FLUIDS IN LOW AND EARTH GRAVITY: *V. M. Emelianov*[1]; A. K. Lednev[1]; [1]Russian Academy of Sciences, Institute for Problems in Mechanics, Prospect Vernadskogo 101, Moscow 117526 Russia

The development of a heated domain induced by a point heat source in supercritical CO2 and SF6 is studied in microgravity and Earth's conditions. New results of the processing of data obtained with the Alice-1 instrument aboard MIR station in 1996 as well as the results of experiments obtained with the instrument on the Earth are presented. A comparison of the initial stage of the development of the heated domain is made for microgravity and Earth's conditions. On the Earth the rate of the rise of the head of the heated plum is found to be independent of T-Tc in a wide temperature range above the critical point but the rate essentially depends on the duration of heating. The final stage of the relaxation of the heated domain in microgravity is also studied.

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SOLIDIFICATION PROCESS ON INDIUM ANTIMONIDE ALLOY THROUGH SUPERCOOLED STATE UNDER ELECTROMAGNETIC LEVITATOR AND MICROGRAVITY CONDITION: *Hideki Minagawa*[1]; Masataka Sasamori[1]; Jiro Nagao[1]; [1]Hokkaido National Industrial Research Institute, Mats. Division, Agency of Indust. and Sci. Tech., Ministry of International Trade and Industry, 2-17 Tsukisamu-Higashi, Toyahira-ku, Sapporo 062-8517 Japan

Supercooled state is usually observed under molten material under containerless system. Furthermore this phenomenon is found to be appeared under microgravity condition, when the partial evaporation of the sample is occurred in ultra-high vacuum system. Because the evaporation gas forces the sample to hover, the noncontact conditions seems to be attained. Microgravity experiment has been performed by 1.3 sec drop tower facility in Hokkaido National Industrial Research Institute (HNIRI). The properties of indium antimonide (InSb), such as energy gap, optical absorbance, and Hall coefficient have been investigated. Semiconductive behavior was observed on In Sb alloy with non-stoichiometric composition near stoichiometry. Temperature dependence of carrier density were compared with that of single crystal InSb(111). Furthermore the solidification experiments through supercooling state under electromagnetic levitator system have been performed. The structure of solidification sample by E-M levitator system was polycrystal or dendrite structure, which were dependent on the supercooled degree.

2:30 PM

AN EXPERIMENT METHOD FOR PREPARING MONOTACTIC ALLOYS IN MICROGRAVITY ENVIRONMENT SIMULATED BY ELECTROMAGNETIC FORCE: *Da Daoan*[1]; Jiang Wanshun[1]; Lu Miao[1]; [1]Lanzhou Institute of Physics, P.O. Box 94, Lanzhou, 730000 PR China

In this paper, a new method is advanced, with which binary monotactic alloys have been prepared on the ground, as a result of elimination of Stockes deposition by means of the interaction between electromagnetic force and melted metal. The experimental apparatus has been established for microgravity simulation by electromagnetic force. It consists of an electromagnet, d.c. current, furnace body, temperature controller, and vacuum system. In the paper, a principle figure and main performance parameters are given. By utilizing the test apparatus, Pb-Zn, Al-Pb, Cu-Pb, Al-In, Zn-Bi, Al-Bi, and triple monotactic alloy Pb-Zn-Bi, have been prepared. The configuration analysis and performance test show that the microcrystals of these samples are uniform in distribution. The ground samples are relatively close to the space-prepared monotactic alloy samples in space in crystal dispersion uniformity. The friction wear-resistant properties of some materials are given.

2:45 PM

DESIGN AND PERFORMANCE OF THE MSL LOW GRADIENT FURNACE (LGF) AND SOLIDIFICATION AND QUENCHING FURNACE (SQF): *A. Lundstrom*[1]; P. Behrmann[1]; H. Lenski[2]; E. Barbier[3]; B. Bonduelle[4]; [1]ESA/ESTEC, P.O. Box 299, AG, Noordwijk NL-2200 The Netherlands; [2]DASA-Dornier, Friedrichshafen Germany; [3]SNECMA-SEP, Villaroche France; [4]SOTEREM, Castanet, Tolosan France

The development of the European Materials Science Laboratory for International Space Station includes two ESA furnace inserts: the Low Gradient Furnace (LGF) and the Solidification and Quenching Furnace (SQF). Both of these have for space furnaces novel design features and performance capabilities, which are discussed in the presentation. The LGF is designed for high temperature operation (1600ϒC) with restricted, well-controlled thermal gradients. It is a multi-zone furnace based on a pyrolytic boron-nitride/pyrolytic graphite heater technology with carbon-carbon diffusers. The LGF performance has been tested in a prototype furnace breadboard. A thermal stability of better than + 0.02 K has been achieved, using a sapphire optical fibre thermometer for heater control. The thermal uniformity of the furnace cavity has been characterised, giving a circumferential isothermality of + 0.5 K. Temperature gradients have been established to be controllable in the range 3-50 K/cm. Test results also include information on the accuracy of temperature sensing and component life-time. The main objective of SQF is to achieve operating temperatures of 1800ϒC and gradients of 150K/cm in a space-compatible furnace design. This challenging task is the topic of an on-going technology development. An innovative self-supported heater design based on carbon-carbon composite or pyrolytic graphite heater elements has been established. Design and manufacturing aspects will be presented; a long-term test of this technology is planned for early 1999.

3:00 PM

LATENT HEAT EFFECTS ON THERMOSOLUTAL CONVECTION IN BRIDGMAN SOLIDIFICATION: *P. Haldenwang*[1]; R. Guerin[2]; [1]Universite de Provence, IRPHE/UMR-CNRS 6594/IMt/Lajetee, Technopole de Chateau Gombert 38, Avenue Joliot-Curie, Marseille Cedex 20 F-13451 France; [2]Universite d'Aix-Marseille III, Laboratoire Matop, URA/CNRS 1530, Faculte des Sciences et Techniques de Saint-Jerome, Case 151, Marsceille Cedex 20 F-13451 France

In upward Bridgman solidification of a binary alloys, the vertical temperature profile being known as stabilising, we address the issue concerning the strength of horizontal thermal gradients that result from the latent heat released by the sample and their influence on solutal

convection. We derive a theoretical estimate which indicates that effects due to heat release increases as the fourth power of aspect ratio (i.e. sample radius reduced with the solutal length) and decreases in inverse ratio to Lewis number squared.

3:15 PM BREAK

3:30 PM

A LIQUID PROPELLANT GAUGING IN MICROGRAVITY ENVIRONMENT AND ITS SIMULATIVE TEST EQUIPMENT ON THE GROUND: *Da Daoan*[1]; Zhang Tianping[1]; [1]Lanzhou Institute of Physics, P.O. Box 94, Lanzhou, 730000 PR China

The effect of microgravity condition on a liquid propellant gauging is analyzed, and one method, named pressure simulation by gas injection(PSGI), was selected for the most suitable technique for gauging liquid propellants on satellites. Our theoretical research on PSGI is presented, and a set of simulative test equipment on the ground, which was developed according to PSGI method, is described in details. This system has the function to simulate liquid propellants gauging under the condition that the propulsion system is either in gear or out of gear. The first part of our experiment results obtained by this equipment has shown that it is possible to get an accuracy higher than 1.0% of the total tank volume with PSGI when the propulsion system is in gear.

3:45 PM

DIAGNOSTIC TOOLS FOR FLUID SCIENCE APPLICATIONS IN MICROGRAVITY: *K. Wozniak*[1]; G. Wozniak[2]; J. Siekmann[1]; [1]University Essen, FB 12, Mechanik, Essen D-45117 Germany; [2]TU Bergakademie Freiberg, Institut fur Fluidmechanik und Fluidenergiemaschinen, Lampadiusstr, 2, Freiberg 09596 Germany

When selecting methods suitable for microgravity fluid physics experiments a variety of diagnostic tools must be considered, because a certain method is very often not compatible with specific experiment and carrier constrains. Furthermore, the application of conventional techniques is characterized by a complex set-up, time consuming adjustments and extensive evaluation procedures. Methods for space borne applications should feature minimum payload requirements and a simple experimental procedure in view of limited operating and crew time. We describe three optical methods in some detail. A digital holographic interferometer, a differential interferometer with Wollaston-prism and the liquid crystal tracer technique exhibiting the following advantages: The experimental set-up has a rather compact design; Extensive alignment adjustment is not required; The sensitivity can be varied in a wide range; Even higher accelerations do not influence the adjustment.

4:00 PM

DOUBLE-LAYERED LIQUID MASS UNDER MICROGRAVITY: Itaru Jimbo[1]; *Masato Takahashi*[1]; [1]Tokay University, Dept. Metall. Eng., 1117 Kita-Kaname, Hiratsuka, Kanagawa 259-1292 Japan

The study of "Double-layered Liquid Mass" under microgravity is undertaken in Tokai University, Japan. The DLM, in which the first spherical liquid mass is covered with the second liquid layer or shell, may be one of the promising material refining and processing procedures, where the reaction occurs at all over the interface between the two liquid phases. This can be well applied in the container-free processes under microgravity. As a preliminary experiment, the DLM consisting of silicone oil and water was successfully produced in a plateau tank facility and the stability of the DLM in this system was carefully investigated. The fundamental factors to control the procedure will be discussed with the calculation result of the total interfacial energy for the separated liquid mass and the DLM. The effect of the application of super sonic wave on the separation of the two liquid phases will also be discussed.

4:15 PM

SOLIDIFICATION OF Al ALLOYS IN MICRO-GRAVITY: *Johan Dahlstrom*[1]; *Hasse Fredriksson*[1]; [1]Royal Institute of Technology, Dept. of Mats. Processing, Dr. Kristinasv. 6, Stockholm S-100 44 Sweden

Solidification of pure Al, Pb and Sn and alloys of Al-Cu, Al-Sn, Pb-Sn has been done in the same experimental set-up in micro-gravity and on earth. The micro-gravity experiments were done on two parabolic flight campaigns. The cooling rates were from 10 C/s to 150 C/s and the size of each sample was around 10 mm3. For Al 2% Cu it was found that the microstructure was finer in the samples solidified on earth. It was also found for Al-alloys that the latent heat was smaller and that the melting point was lower in earth based compared to micro-gravity experiment at similar cooling rates. This was explained by the creation of more excess vacancies during solidification on earth compared to solidification in micro-gravity. The number of vacancies and the phase diagram was calculated for excess vacancies.

4:30 PM

GROWTH OF II-VI SOLID SOLUTIONS IN THE PRESENCE OF A ROTATING MAGNETIC FIELD: *D. C. Gillies*[1]; S. Motakef[2]; M. Dudley[3]; R. Matyi[4]; H. Volz[4]; [1]NASA/Marshall Space Flight Center, Huntsville, AL 35812; [2]Cape Simulations Inc., Newton, MA 02458; [3]State University of New York at Stony Brook, Stony Brook, NY 11794; [4]University of Wisconsin-Madison, Madison, WI 53706

The application of a rotating magnetic field (RMF) in the frequency range 60-400 Hz and field strength of 2-8 mT to crystal growth has received increasing attention in recent years. To take full advantage of the control of fluid flow by the forces applied by the field, the liquid column must be electrically conducting. Also, the application of RMF to the directional solidification of a column of liquid can result in complete mixing in the resultant solid. Thus, the technique of RMF is suited to solvent zones and float zones where the composition of the liquid is more readily controlled. In the work we report on, numerical modeling has been applied to II-VI systems, particularly tellurium based traveling heater techniques (THM). Results for a spectrum of field strengths and acceleration levels will be presented. These show clearly the effects of competing buoyancy forces and electromagnetic stirring. Crystals of cadmium zinc telluride and mercury cadmium telluride have been grown terrestrially from a tellurium solvent zone. The effects of the RMF during these experiments will be demonstrated with micrographs showing etch pits, white beam x-ray synchrotron topographs and triple axis x-ray diffraction.

4:45 PM

SURFACE TENSION AND VISCOSITY MEASUREMENTS IN MICROGRAVITY: SOME RESULTS AND FLUID FLOW OBSERVATIONS DURING MSL-1: R.W. Hyers[1]; *G. Trapaga*[2]; and M.C. Flemings[2]; [1]NASA-MFSC, Mail Code EC76, Huntsville, AL 35812; [2]Department of Materials Science and Engineering, Massachusetts Institute of Technology, 77 Massachusetts Ave. Rm. 8-101, Cambridge, MA 02139

The viscosity of a liquid metal was successfully measured for the first time by a containerless method, the oscillating drop technique. This method also provides a means to obtain a precise, non-contact measurement of the surface tension of the droplet. This technique involves exciting the surface of the molten sample and then measuring the resulting oscillations; the natural frequency of the oscillating sample is determined by its surface tension, and the damping of the oscillations by the viscosity. These measurements were performed in TEMPUS, a microgravity electromagnetic levitator (EML), on the Space Shuttle as a part of the First Microgravity Science Laboratory (MSL-1), which flew in April and July 1997 (STS-83 and STS-94). Some results of the surface tension and viscosity measurements are presented for Pd82Si18. Some observations of the fluid dynamic characteristics (dominant flow patterns, turbulent transition, cavitation, etc) of levitated droplets are presented and discussed together with magnetohydrodynamic calculations, which were performed to justify these findings.

ALUMINA AND BAUXITE: Alumina Process Developments

Sponsored by: Light Metals Division, Aluminum Committee
Program Organizer: Joe Anjier, Kaiser Aluminum & Chemical Corporation, P.O. Box 3370, Gramercy, LA 70052 USA

Tuesday PM Room: 6E
March 2, 1999 Location: Convention Center

Session Chair: Travis J. Galloway, Reynolds Metals, Global Bauxite/ Alumina Business Unit, Richmond, VA USA

2:00 PM

NEW WATER-CONTINUOUS RED MUD FLOCCULANTS FOR THE BAYER PROCESS: *Everett Charles Phillips*[1]; [1]Nalco Chemical Company, Alumina Process Chemicals Group, Mining and Mineral Processing Division, One Nalco Center, Naperville, IL 60563-1198 USA

A new family of water-based red mud flocculants has been developed for use in the Bayer Process. There are several key advantages of this Water-Continuous Flocculant technology compared to dry and oil-based latex red mud flocculants. These include improvements in liquor clarification performance and advantages related to the form of these products. This paper presents the developments to date, including results from plant evaluations, demonstrating the utility of this new technology for clarifying Bayer Process red mud slurries.

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BAYER PROCESS ZINC REMOVAL RESEARCH: Gan Guoyao[1]; *Wang Longzhang*[1]; Yang Shijie[1]; [1]Pingguo Alumina Plant, Pingguo, Guangxi 531400 China

Pingguo bauxite contains a high content of zinc. Zinc removal technology for the Pingguo plant was researched. This paper presents the results of this study. The effect of removing zinc is not good when adding as many moles of sodium sulfide as zinc. When an excess of sodium sulfide is added, the content of zinc in the pregnant liquor decreased greatly but the silica and iron increased significantly. Increased retention time and air agitation improved the process and most of the zinc was removed and settled into the red mud. The paper describes the development of this powerful process.

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THE CHEMISTRY OF SOLID-LIQUID CALCINATION(SLC): *Helene Boily*[1]; Flor Campa[2]; Kirsten Theisen[3]; [1]Alcan International, Ltd., P.O. Box 1250, 1055 Mellon Blvd., Jonquiere, Quebec G7S4K8 Canada; [2]ALCOAO Inespal, Apartado 71, San Ciprian, Lugo 27890 Spain; [3]F. L. Smidth & Company, Vigersley Alle 77, Valby DK2500 Denmark

Commissioning of the 120 T/D prototype SLC unit began in late summer 1998 at San Ciprian, with a feed slurry mixture containing salt cake (crystallized sodium salts from the Bayer process), bauxite slurry and concentrated spent liquor. The parameters used to control the process will be reviewed, together with the chemical and physical properties of the feedstock, the intermediate phases and end products of the process.

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ALUMINA PRODUCTION FROM DIASPORIC BAUXITES: *Eric Lavalou*[1]; Bernard Bosca[2]; Odysseas Keramidas[2]; [1]Aluminium Pechiney, BP42, 13541 Gardanne, Cedex France; [2]Aluminium de Greece, Paralia Distomon, 32003, Saint Nicolas, Beotie Greece

Diasporic minerals represent only a small part of the world deposits in metallurgy grade bauxites. Nevertheless, these materials are strategic for global commercial exchanges of some countries, like Greece or People's Republic of China for example. Following an overview on geology, main locations, and characteristics of diasporic bauxites, will be discussed: chemical and technological problems during their use in Bayer process; process and technology efficiency in some industrial realizations; and current developments, and optimization prospects to break through present yield limitations that is 97% (digestion) and 90 gpl (precipitation).

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SETTLER THROUGHPUT INCREASE AT ALUMINIUM DE GRECE REFINERY: *X. Perrier*[1]; B. Benoit[2]; P. Dountsis[1]; [1]Aluminium Pechiney, Direction de la Technologie Alumine, BP 54, Gardanne 13541 France; [2]Aluminium Pechiney, Direction de la Rocherche et du Development, BP 54, 13541 Gardanne, Cedex France

Aluminium de Grece has five primary mud settlers, four flat bottomed and one conical bottomed. These settlers have been operated on starch based flocculants since plant start up. The maximum overflow rate has been approximately 0.6m^3/h.m^2 corresponding to 50 kg/h.m^2 mud throughput. In order to get additional washing stages and to reduce mud residence time, several synthetic flocculant strategies were investigated. The target overflow rate was 1.2 m^3/h.m^3. During industrial tests, the target was exceeded with hydroxamate both with and without starch. With polyacrylamide and starch it was difficult to simultaneously control clarity and rake torque. Hydroxamate dosage was progressively optimized and presently operation with only two settlers on line is considered.

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ALUMINA TRIHYDRATE PRECIPITATION PARTICLE SIZE CONTROL: *Bret Garner*[1]; Arnaud Soirat[1]; Benoit Cristol[2]; [1]Queensland Alumina, Ltd., Parsons Point, Gladstone, Queensland 4680 Australia; [2]Alumina Research & Development Centre, Aluminium Pechiney, Gardanne Cedex, France

By employing a reliable and comprehensive set of sensors and appropriate actuators according to Pechiney Particle Size Distribution Control strategy, a new methodology has been implemented to stabilize and optimise particle size distribution within Queensland Alumina's precipitation circuit. The new methodology, based on quantitative control of fines through adjustment of agglomeration set points, allows elimination of the detrimental consequences of sub-optimal seed size control, such as: reduced circuit seed surface area leading to reduced yield; increased probability of nucleation explosions; reduced pregnant liquor flows and/or seed charge due to unsustainable fines inventory build up, and swings in alumina product quality. This paper examines the impact of this sub-optimal seed size control on circuit performance and benefits derived from the improved control to date.

5:30 PM INVITED PAPER

IMPROVEMENT OF FLOWSHEET OF ALUMINA PRODUCTION IN SODA-LIME SINTERING PROCESS: *Shang-guan Zheng*[1]; Zhong-yu Yang[1]; Shen-xing Hu[2]; An Luo[2]; [1]Central South University of Technology, Dept. of Metall., Changsha, Hunan Province 410083 PR China; [2]Shandong Aluminum Corporation, Corporation Office, Zibo, Shandong Province 255052 PR China

An improved technology in the present work is proposed that pregnant liquor from sinter leaching in soda-lime sintering process is subjected to carbonization and thus obtained raw Al(OH)3 (high silica content) is processed with very simple Bayer process instead of multi-desilication process. With the new technology, sandy alumina with high quality could be produced in sintering process; the amount of sinter could be decreased by about 0.5 t/t-Al2O3; process control is easier than before; the consumption of CO2 gas for carbonization is only increased by 3.65%; the increased operation cost of inserted simple Bayer process could be completely compensated by the cost of the oringinal desilication operation which has been cancelled in the new technlogy. The production cost with the improved technology could be decreased by 82.87 yuan/t-Al2O3 and the output of alumina would be increased by 75 000 tons/year. Keywords: high silica bauxite, soda-lime sintering process, sinter leaching, purification of raw Al(OH)3

ALUMINUM REDUCTION TECHNOLOGY: Control of Reduction Lines

Sponsored by: Light Metals Division, Aluminum Committee
Program Organizers: Georges J. Kipouros, DalTech, Dalhousie University, Dept. of Mining & Met. Eng., Halifax, NS B3J2X4 Canada; Mark P. Taylor, Comalco Aluminium, Ltd., Brisbane, Queensland 4001 Australia

Tuesday PM Room: 6F
March 2, 1999 Location: Convention Center

Session Chair: Pierre Homsi, Aluminium Pechiney, Laboratoire de Recherches des Fabrications, St. Jean De Maurienne Cedex BP114 733 France

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REDUCTION CELL AUTOMATION: IMPROVEMENTS OF THE ALUMINIUM SMELTER IN POLAND: E. Bugzel[2]; J. Galek[3]; A. Jozwiak; R. T. Mourão[1]; *C. M. Ritter*[1]; [1]ATAN Automation Systems, Aluminium Division, Rua Pernambuco 353, sl. 811, Funcionários, Belo Horizonte, Minas Gerais 30130-150 Brazil; [2]Huta Aluminium KONIN S A, Development and Modernization of Electrolysis Dept., ul. Hutnicza 1, Konin 62510 Poland; [3]Huta Aluminium KONIN S A, Production Dept., ul. Hutnicza 1, Konin 62510 Poland; Huta Aluminium KONIN S A, Power and Mechanical Dept., ul. Hutnicza 1, Konin 62510 Poland

This paper describes the performance and operational improvements achieved by Huta Aluminium Konin after the adoption of a new automation system and operational strategies. An historical overview of the previous control system is presented. Next, the features and the topology of the new automation system are described. The results obtained due to the new configuration and the operational interaction with the automation system are then presented. Concluding the paper, the immediate benefits and the medium and long term advantages related to these changes are discussed.

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ELIMINATING THE ANODE EFFECTS: *R. G. Haverkamp*[1]; [1]Massey University, Institute of Technology and Eng., Private Bag 11222, Palmerston North New Zealand

The anode effect in the production of aluminium by the Halt-Heroult process is a well known but poorly understood effect. In this paper the literature on the anode effect is reviewed and parallels drawn with electrode phenomena in other processes. In industrial cells the anode effect is tolerated as a check on alumina levels to reduce the possibility of sludging however it has the negative consequences of increased CF_4 emissions, cell overheating, reduced production and increased energy consumption. It is proposed that it is desirable to eliminate anode effects completely, with a possible accompanying decrease in sludging, by more careful control of dissolved alumina levels and bath temperature.

3:05 PM
POINT FEEDING FOR CONSTANT ALUMINA CONCENTRATION IN SÖDERBERG CELLS: *R. T. Mourão*[1]; a. fERNANDES[1]; E. Castro[2]; [1]ATAN Automation Systems, USC, R. Pernambuco, 353, Funcionários, Belo Horizonte, Minas Gerais 30130-150 Brazil; [2]CBA, R. Moraes 347, Aluminio, Brasil, 18125-000

This paper presents an algorithm for alumina point feeding in Söderberg cells at CBA, Companhia Brasileira de Alumínio. The developed algorithm is a variation of the "demand feeding" algorithm, where the pot is fed according to its demand of alumina. The main objective of the algorithm developed is to keep alumina concentration in the bath as constant as possible. The revised operational procedures and the improvements in the pot line overall efficiency due to the point feeding are presented and discussed.

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IMPROVED CONCEPT OF ALUMINA-FEEDING STRATEGY: *K. Hofenbitzer*[1]; [1]VAW Aluminium-Technologie GmbH, Georg-von-Boeselager-Str.25, Bonn 53117 Germany

The state-of the art Point-Feeding System recently developed by VAW Aluminium-Technologie GmbH (VAW-ATG) has already been successfully installed in all potlines at VAW's Rheinwerk Smelter. The latest Alumina-Feeding technology gives some telling advantages: compressed air consumption is significantly reduced; immersion of the breaker in the molten cryolite is reduced to an absolute minimum; possible irregularities will be indicated by alarms. The point feeders are continuously controlled via ELAS, the pot-controller. ELAS, the basic element of the Alumina-Feeding technology enables all personnel involved in aluminium reduction to control the whole modus operandi not only of crust breaking and feeding components. An up-to-date graphical user interface in conjunction with the accompanying ELAS software package allows the operator to communicate easily with his potline form anywhere in the world.

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AUTOMATIC DETERMINATION OF METAL HEIGHT IN ELECTROLYSIS CELLS: *G. A. Guðmundsson*[1]; [1]Icelandic Aluminium Company, Ltd., Eloctrolysis, Straumsvík, P.O. Box 244, Hafnarfjörður IS-222 Iceland

A reliable measurement of metal height to decide tapping amount of pots has been badly needed in the aluminium industry. In this paper a method for automatic determination of metal height is described. The method is based on calculation from insertion height of anodes and the height of the anode beam from a beam position transducer. The determination can be made more accurate by correcting for deviation from various setpoints according to known correlations. Such corrections are pot voltage, bath temperature and bath composition. At the Icelandic Aluminium Co., Ltd. this method has been used since spring 1997. The method has stabilised tapping amount, fluoride concentration and temperature. It was implemented with the existing process control system, which is based on Pot Control Units from ALESA Alusuisse Engineering, Ltd. No extra transducers had to be installed. Bath height and metal measurement is also done manually as the bath height is still needed. The tapping amount is decided by the automatic determination of the metal height but is occasionally adjusted according to the manual measurement.

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THE PECHINEY SEMI-CONTINUOUS & AUTOMATIC MEASUREMENT DEVICE (CMD), A NEW TOOL FOR AUTOMATIC MEASUREMENTS: *O. P. Bonnardel*[1]; P. Homsi[1]; [1]Aluminium Pechiney, LRF, B.P.114, 73303 Saint-Jean-De-Maurienne Cedex, Savoie France

For many years, Aluminium Pechiney has been developing advanced software tools in pot process control, which has become one of the cornerstones of Pechiney's technology. The effectiveness of this control depends on the quality of the measurements. Except for pot voltage and potline amperage, measurements are taken manually, which means high operating costs, low frequency and lack of accuracy. The purpose of this paper is to present the new Pechiney patented tool for taking automatic measurements of bath temperature and bath level. First, the inherent advantages of automatic measurements over manual measurements are summarized. We then describe the semi-Continuous & automatic Measurement Device (CMD) and its integration in the process control chain, i.e. the pot micro and the potline supervisory systems. Finally, we present quantified improvements in operating values and the overall profitability of the device.

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REAL TIME SIMULATOR TOOL FOR TRAINING AND DEVELOPMENT IN REDUCTION CELLS: *A. Meghlaoui*[1]; Y. A. Mohamed[1]; B. Jolly[1]; [1]Dubai Aluminium Company, Ltd., (DUBAL), Technology Development, P.O. Box 3627, Dubai United Arab Emirates

A computer simulator of an electrolytic cell has been constructed at Dubal. The mathematical model, already adapted using plant data, is controlled by a pot control unit (PCU). An adequate software-hardware

environment has been developed to receive the line current signal from the plant data network and to establish a reliable data exchange between the PCU and the cell simulator. This real time simulator serves as a tool for training, development of pot control strategies and testing the functioning of the whole system. In this paper several features related to the connection of the PCU to the "soft cell" and running real time simulation are presented and discussed in details to help in overcoming difficulties encountered in this integration process.

ANALYTICAL TECHNOLOGY IN THE MINERAL INDUSTRIES: Analytical Methods for Acid Rock Drainage Prediction

Sponsored by: Extraction & Processing Division, Process Mineralogy Committee; ASTM Subcommittee E01.02

Program Organizers: Louis J. Cabri, CANMET, Ottawa, Ontario K1A 0G1 Canada; Charles H. Bucknam, Newmont Metallurgy Services, Englewood, CO 80112 USA; Steven L. Chryssoulis, Amtel, London, Ontario N6G 4X8 Canada; Rebecca A. Miller, Minekeepers, Phoenix, AZ 85014 USA; Emil Milosavljevic, Lakewood, CO 80227 USA

Tuesday PM Room: 7A
March 2, 1999 Location: Convention Center

Session Chairs: Rebecca A. Miller, Minekeepers, Phoenix, AZ 85014 USA; C. Mark Wallis, Hydrometrics, Tucson, AZ 85741

2:30 PM INVITED PAPER

MODELING REACTIVE SOLUTE TRANSPORT FROM HISTORIC WASTE ROCK TO RECEIVING GROUNDWATER IN THE ROBINSON DISTRICT, ELY, NEVADA.: *Andy Davis*[1]; G. Fennemore[1]; J. Anderson[1]; S. Okeson[1]; C. Byrns[2]; [1]Geomega, Geochemistry, 2995 Baseline Rd., Suite 202, Boulder, CO 89319 USA; [2]BHP Robinson, Ely, NV 89319 USA

Groundwater flow and solute transport modeling was conducted to evaluate the environmental impacts of historic waste rock dumps and related seeps in the Robinson Mining District, Ely, Nevada. The objectives of the investigation were to: 1) understand the incremental impact of historic mining activities on groundwater; 2) identify which waste rock dumps, if any, contribute to local groundwater chemistry; 3) determine if seeps and springs affect groundwater at the local or regional scale; and 4) assess the spatial extent of mine-affected groundwater. The rate of pyrite oxidation in waste rock dumps was determined using the WROC-2D code, in conjunction with geochemical characterization data collected from waste rock dumps across the site. Waste rock dump oxidation was predicted using data from the waste rock characterization calibrated to measured oxygen and temperature profiles in the dumps. Then 4 well-benchmarked codes were coupled to determine flux from the waste rock dumps and seeps. HYDRUS_2D (unsaturated zone flow and transport), was coupled to MODFLOW (saturated zone flow), MT3D96 (saturated zone solute transport), and PHREEQC (equilibrium reaction chemistry through the vadose and saturated zones). The 60-year simulations demonstrated that sulfate, the most mobile constituent, remains close to local sources within the Robinson Mining District, including all historical source area locations where groundwater impacts are predicted by releases at the surface. The complex structural geology and metamorphism in the Robinson District and the depths to the regional aquifer have resulted in no impacts from historic mine operations to the deep carbonate aquifers within the Robinson Mining District. Laterally, groundwater flow from the mine area into the adjoining hydrogeologic provinces is recalcitrant due to numerous hydraulically impeding faults and low conductivity rocks. Solute groundwater transport simulations demonstrated that even sparingly reactive solutes, such as sulfate, have not migrated more than 1600 feet laterally from the potential historic source areas.

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ROLE OF SILICATES IN THE COMPOSITIONAL EVOLUTION AND NEUTRALIZATION OF Fe- AND Mg-SULPHATE TYPE WATERS IN WAITE-AMULET TAILINGS, CANADA: *John L. Jambor*[1]; H. Wayne Nesbitt[2]; [1]Leslie Investments, Ltd., 316 Rosehill Wynd, Tswwassen, British Columbia V4M 3L9 Canada; [2]University of Western Ontario, Dept. of Earth Sciences, London, Ontario N6A 5B7 Canada

Oxidative dissolution of pyrrhotite is largely responsible for the sulphate-rich waters of the vadose in Waite-Amulet tailings. Although the shallowest of the sulphate-rich waters are Fe-SO4 type, they evolve to Mg-SO4 type, near-neutral waters within 1 to 2 metres of the tailings surface. The mafic silicate minerals are the only Mg-bearing phases present in sufficient quantity to account for the abundance of Mg in these solutions and to neutralize the amount of acid produced. A chemical weathering methodology demonstrates that the Mg-silicates exert major influence on the evolution of these waters. Relative rates of reaction of primary minerals (quartz, feldspars, micas, pyroxenes and amphiboles) can be deduced by comparison of modal abundances in the vadose and phreatic zones of the tailings. The relative rates of sulfides, phyllosilicates, pyroboles (pyroxenes and amphiboles), feldspars and quartz weathering in the vadose zone are 10:4:2:1:1. The evolution of pore waters from Ca-Na-HCO3 type (emanating from the crushed limestone cover), to saline Fe-SO4 type and finally to Mg-SO4 type waters in the vadose zone can be summarized in three reactions. Two represent pyrrhotite and pyrite oxidative dissolution, with the former being far more important to the evolution of these waters than the latter. The major neutralizing reaction involves reaction of Mg-bearing phyllosilicates and pyroboles with the acidic waters of the tailings. Their high reactivity suggests mafic minerals have significant intermediate and long-term neutralizing capacity. Their effects should be considered when evaluating the long-term costs of mine waste treatment.

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THE EFFECT OF ARID CONDITIONS ON PYRITE OXIDATION KINETICS: *Andy Davis*[1]; C. Neller[1]; G. Fennemore[1]; [1]Geomega, Geochemistry, 2995 Baseline Rd., Suite 202, Boulder, CO 89319 USA

The primary factor influencing wall rock leachate chemistry is the propensity for sulfide minerals in the rock to oxidize and release solutes when leached. Typically, pit lake prognostications have relied upon humidity cell tests to derive possible wall rock leachate chemistry. However, these tests unrealistically simulate conditions in Nevada because moist air is employed in the oxidation step for 50% of the time, and in practice the rock material rarely dries out completely during the drying cycle. Further, the humidity cells only incorporate the <2mm fraction, while in reality there is a large range of particle sizes in the ultimate pit surface wall rock. Consequently, a more representative method was sought to determine wall rock leachate chemistry. 47 humidity cells were run on material with a wide range of NCVs (e.g., -7 to +16 for the field oxidation experiment, and -9 to +25 for the humidity cell test). Additionally, samples were crushed and sieved to 2-4 mm, 4-16 mm, and 16-64 mm to assess particle size effects. The 16 bucket leachate tests used 800 g of each of 15 rock samples collected from the pit wall that were splits of those rocks used in the humidity cell tests. Another bucket, which did not contain any rock sample, was set up as a control to collect site precipitation. Runoff from the bucket tests was collected six times following precipitation events and the volume of runoff following each event was measured to allow normalization of the field and laboratory data sets. The results demonstrate that the field oxidation tests generated lower solute concentrations than those in the analogous humidity cell tests, with the most noticeable differences observed in the acid-generating rocks where the humidity cells overestimated field leachability by up to an order of magnitude, while increasing particle size resulted in reduced leachate solute concentrations in both the field and humidity cell tests.

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4:05 PM INVITED PAPER

MANAGEMENT OF POTENTIALLY ACID FORMING OVERBURDEN AT KPC COAL MINE, INDONESIA: *Warwick Stewart*[1]; Dan Michaelsen[1]; [1]PT Kaltim Prima Coal, Mine Office, Sangatta, East Kalimantan Indonesia

PT Kaltim Prima Coal (KPC) is a large-scale truck and shovel coal mining operation situated in the tropical equatorial region of East Kalimantan, Indonesia. The operation produces 15 million tonnes of coal and over 120 million bank cubic meters of overburden annually. Approximately 35 percent of the overburden is classified as potentially acid forming and therefore there is a potential to produce large volumes of acid drainage and large areas of acid spoil. Management of acid rock drainage (ARD) is required for both overburden dumps currently under construction, and for those constructed prior to ARD being identified as an issue. A modified field net acid generation (NAG) test procedure has been developed at KPC for identification and segregation of overburden geochemical types. The development and field application of the NAG procedure is presented in a companion paper. KPC aims to prevent acid production in dumps by covering potentially acid forming spoils with materials identified as non-acid forming. The covers, built to engineering standards, minimise the flux of oxygen and water to pyritic spoils, thereby controlling the oxidation reaction to meet a design target acid sulphate generation rate of less than 10 tonnes SO4/ha/yr. Cover designs and cover material vary according to stability, materials availability, equipment availability and cost effectiveness. This paper discusses the ARD management strategies and operational procedures adopted by KPC to effectively manage potentially acid forming overburden.

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IDENTIFYING POTENTIALLY ACID FORMING OVERBURDEN TYPES USING A FIELD NAG TEST PROCEDURE AT KPC COAL MINE, INDONESIA: *Clayton L. Rumble*[1]; Stuart D. Miller[1]; [1]Environmental Geochemistry International Pty, Ltd., 81A College St., Balmain, NSW 2041 Australia

A field net acid generation (NAG) test procedure has been utilised onsite to identify, classify and map potentially acid forming overburden at the KPC (PT Kaltim Prima Coal) coal mining operation situated in the tropical equatorial region of East Kalimantan, Indonesia. The field procedure involves routine use of a calibrated, site specific NAG test (rapid oxidation test using hydrogen peroxide) which has a turn-around time of less than 24 hours and requires minimal sample preparation. It is used on geological drill-hole samples, for forward planning and overburden management; blast-hole samples, for day-to-day planning and overburden scheduling; and final dump surface samples, for verification testing. This operational monitoring program has been in use at KPC for the past four years. Calibration and implementation of the field procedure has involved validating the NAG test using conventional acid-base accounting techniques, producing an overburden geochemical classification scheme, optimising laboratory and sample preparation procedures, and ongoing quality management. This paper presents background theory and practical application in a case study format.

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USE OF THE NET ACID GENERATION PH TEST FOR ASSESSING RISK OF ACID GENERATION: *William M. Schafer*[1]; Ed Spotts[1]; Freddy Guard[1]; Michael Brewer[1]; [1]Schafer & Associates, P.O. Box 6186, Bozeman, MO 597771-6186 USA

The net acid generation (NAG) pH analysis is a method that allows rapid assessment of the acid generation risk of rock samples. This method is useful because it is simple, effective, rapid, and can be conducted at mine assay labs. The NAG pH test is particularly effective for operational testing programs used to classify, selectively handle, and route potentially acid generating waste rock. The NAG pH procedure is based on a 24-hour oxidation of a pulverized rock sample with hydrogen peroxide and subsequent measurement of the sample's pH. The 24-hour pH measurement is called the sample's "NAG pH" value. The 24-hour duration provides time for sulfuric acid to be produced through oxidation of pyrite contained in the sample, followed by dissolution and neutralization of the acid by carbonates and other rapidly-reacting neutralizing minerals present in the sample. If the NAG pH is below a critical value, determined empirically, then the sample has the potential to generate acid in the field. If the NAG pH is above this value, then it is considered a non-acid generator. The critical NAG pH value is typically within the range of 3 to 4.5. However, the exact relationship between NAG pH and potential acid generation should be determined individually for each rock type at each mine site, based on comparison with results of acid base accounting, humidity cell tests, and mineralogical analyses for each rock type. Case studies of the calibration and use of the NAG test for predicting ARD risk are described in this report. NAG pH compares favorably with results of 20-week humidity cell tests. In addition, it has been used successfully for mines with high sulfide-high carbonate mineralogy, and for low sulfide-low carbonate systems.

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ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY (EIS) TECHNIQUE FOR THE PREDICTION OF ACID MINE DRAINAGE POTENTIAL OF WASTE ROCKS: *Manoranjan Misra*[1]; *X. Su*[1]; Indira Chatterjee[3]; [1]University of Nevada, Reno, Dept. of Chem. & Metall. Eng., MS-170, Reno, NV 89557 USA; [3]University of Nevada, Reno, Dept. of Elect. Eng., MS-260, Reno, Nevada 89557 USA

The conventional methods to assess AMD potential of the waste rocks and tailings are based on wet chemistry and leachability tests. Recently, Electrochemical Impedance Spectroscopy (EIS) has been used to predict the AMD potential of the waste rocks and sulfide tailings. The EIS method is non-evasive and rapid. This method can be used for different types of reactive tailings and rocks.

AUTOMOTIVE ALLOYS III: Session IV — Applications

Sponsored by: Light Metals Division, Aluminum Committee
Program Organizer: Subodh Das, ARCO Aluminum Company, P.O. Box 32860, Louisville, KY 40232 USA

Tuesday PM Room: 3
March 2, 1999 Location: Convention Center

Session Chairs: Subodh K Das, ARCO Aluminum, Inc., Louisville, KY 40232 USA; Andrew M. Sherman, Ford Motor Company, Ford Research Laboratory, Dearborn, MI 48121-2053 USA

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DEVELOPMENT AND APPLICATION OF A MODIFIED 319 SEMI-SOLID ALUMINUM ALLOYS TO REPLACE CAST IRON AUTOMOTIVE PARTS: *S. C. Bergsma*[1]; [1]Northwest Aluminum Company, 3313 West Second St., The Dalles, OR 97058 USA

A major manufacturer of automotive seat belt components was investigating various aluminum alloys to replace a critical cast iron seat belt part. Several cast aluminum alloy parts were tested and failed but the part fabricated from 6061.T6 was approved. However, the cost of forging and machining a 6061 part was deemed prohibitive. Their first semi-solid test parts were formed from alloy 357 but a few of these parts failed. Subsequently, a modified 319 alloy (designated DF-53) was tested and approved and has been in production for over a year. The ingot used to form these parts relies on Semi Solid Thermal Transformation (SSTT) during induction heating to obtain a spherical structure suitable for semi-solid forming. Finished T6 parts from DF-53 have properties approaching 6061.T6. This report covers the ingot technology and the DOE to determine the best T5 and T6 practices for DF-53.

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MECHANISMS OF SOLDERING IN HIGH PRESSURE DIE CASTING OF ALUMINIUM ALLOYS: *Zhan Wen Chen*[1]; Mahnaz Z. Jahedi[1]; [1]CSIRO, Manuf. Sci. and Tech., Corner Raglan and Albert Sts., Preston, Victoria 3072 Australia

High pressure die casting (HPDC) is a widely used manufacturing process for mass production of near net shape automotive components of aluminium alloys. Soldering is an important die failure mode in HPDC

but the metallurgy processes of soldering are not clear. In this study, HPDC soldering experiments have been conducted using core pins as soldering targets. Due to heat loss in the process, the soldering reactions in the die cavity occurred at temperatures equal or below the liquidus temperature of the cast alloy. Local solidification time was found to be the main determining factor for the severity of soldering. Hence, in thicker sections of the casting, the pins came in contact with the solidifying alloy longer during a casting cycle than thinner sections and therefore required less cycles to solder. Soldering started with the formation of localized intermetallic particles accompanied by the build-up of solidified cast alloy. The soldered layer developed through the growth of these intermetallics via a solid state reaction together with coarsening of the phases in the cast alloy layer adjacent to the soldering intermetallics. The fracture path separating the casting and the soldered pins during casting ejection was usually in the cast alloy rather than inside the intermetallic layers. This may be related to the lower mechanical properties of the cast alloy adjacent to the intermetallic layers.

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FRICTION STIR WELDING MAGNESIUM ALLOYS: *G. Kohn*[1]; S. Antonsson[2]; A. Munitz[3]; [1]Rotem Industries, Ltd., Beer-Sheva Isreal; [2]ESAB AB, Ltd., Lexa Sweden; [3]NRCN, Beer-Sheva Israel

In the frame-work of the Israeli Consortium for the Development of Magnesium Technologies, a large variety of joining methods are being studied and their suitability for magnesium alloys is examined. Among others, a relatively new method called Friction Stir Welding (FSW) was studied. The integrity and properties of the FSW specimens was investigated using conventional destructive and non-destructive testing methods. It was found that Mg type AZ91D cast alloy can be welded using the FSW method with negligible amount of defects. A complex microstructure of the weld area was observed which was comprised of three different type of zones: I. Molten and resolidifed areas with a central heavily stirred zone and a thin molten layer at the top of the welded plates; II. Areas exhibiting evidence of severe plastic flow, that include also partially melted and recrystallized zones; III. Heat affected zones. The severe plastic deformation and rapid solidification involved in FSW resulted in fine microstructure welds with enhanced mechanical properties compared to those of the parent material.

3:00 PM

ROLL FORMING OF AXISYMETRIC COMPONENTS OF ALUMINUM ALLOYS II: APPLICATION TO 7000 SERIES AND CAST ALUMINUM ALLOYS: *C. K. Syn*[1]; [1]Lawrence Livermore National Laboratory, Livermore, CA 94551 USA

A unique roll forming technology that permits complex axisymmetric components, such as automotive wheels and turbine disks, to be formed in a single forming operation, has been developed by two Russian institutes, the Russian Federal Nuclear Center, Institute of Technical Physics and the Institute for Metals Superplasticity Problems. The roll-forming process offers opportunities to manufacture high strength components in continuous, economical operations. In addition, the process eliminates the need to manufacture the matching die sets that are required in conventional forging operations. This process was used to fabricate automobile wheels from a Russian AVT alloy, a 6010 aluminum alloy equivalent, as reported in the Symposium on Automotive Alloys II. In the present report, application of the process to high-strength 7000 series aluminum and cast aluminum alloys will be described. The process included steps of isothermal compression of the initial blanks, isothermal forging of the blanks into preforms, and final isothermal roll forming of preforms into wheel shapes. The microstructure and mechanical properties were evaluated for the finished wheels, preforms, and initial blanks by metallography and tensile testing at elevated temperatures.

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TENSILE AND FATIGUE PROPERTIES OF A356 AND A357 SQUEEZE AND SEMI-SOLID CASTINGS: Gautham Ramachandran[1]; *Robert M. Aikin*[1]; [1]Case Western Reserve University, Dept. Mats. Sci. & Eng., 10900 Euclid Ave., Cleveland, OH 44106 USA

The tensile and axial fatigue properties of A356 (Al-7Si-0.35Mg) and A357 (Al-7Si-0.55Mg) produced by both the squeeze and semi-solid casting processes have been examined. The samples tested were all taken from commercial automotive castings. Due to the lack of porosity and other large defects, very high tensile elongation's and very good fatigue properties were exhibited by all of the samples. The influence of microstructure on the tensile and fatigue properties of these samples will be discussed with respect to the significant differences in Si distribution produced by the squeeze and semi-solid casting processes.

4:10 PM

OPTIMISATION OF QUALITY OF HIGH PRESSURE DIE CAST MAGNESIUM ALLOYS: *A. K. Dahle*[1]; S. Sannes[2]; D. H. St. John[1]; H. Westengen[2]; [1]The University of Queensland, Dept. of Mining, Minerals and Mats. Eng., CRC for Alloy and Solidification Technology (CAST), Brisbane, Queensland 4072 Australia; [2]Norsk Hydro Research Centre, Porsgrunn Norway

Die cast magnesium components are finding increased use worldwide because of the excellent castability and properties that magnesium alloys can offer. Because of the excellent flow characteristics of molten magnesium, high-pressure die casting of thin-walled components is particularly suitable with magnesium. The use of magnesium die castings in automotive applications is currently increasing rapidly with new applications including components such as instrument panels, steering wheels, transmission housings, door frames and seat frames. These applications require optimisation of the quality and performance of the castings. It has been found that bands of porosity or segregation which follow contours parallel to the surface of the casting are formed under certain casting conditions in thin-walled magnesium high pressure die castings. The presence of this type of defect can have a significant effect on the mechanical properties. The present paper provides a rationale for understanding the origin of these defect s which is related to the solidification behaviour, the mushy zone rheological properties and the filling pattern of the casting with associated shearing of the mushy zone. The effect of varied casting conditions on the casting integrity and the appearance of the bands is investigated and rationalized by the theory. Methods to optimise the process parameters to control the occurrence of the banded defects and thereby optimise the quality of high pressure die cast magnesium components, are outlined.

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FATIGUE BEHAVIOR OF A356.2 CASTING ALLOYS WITH GRADIENTS IN DENDRITE ARM SPACINGS AND POROSITY: Bin Zhang[1]; David R. Poirier[1]; *Weinong Chen*[2]; Q. T. Fang[3]; [1]University of Arizona, Mats. Sci. and Eng., AME Bldg. 119, Tucson, AZ 85721 USA; [2]University of Arizona, Aerospace and Mech. Eng., AME, Tucson, AZ 85721 USA; [3]Alcoa Technical Center, Alcoa Center, PA 15069-0001 USA

Low and high cycle fatigue lifes of A356.2-T6 cast aluminum alloy with various secondary dendrite arm spacings (DAS, 15um-55um) and porosity (10um-500um) levels in the microstructure were measured under both axial and bending loading conditions at strain/stress ratios of -1 and 0.1. SEM and optical microscopy observations revealed that high-cycle fatigue cracks initiated at near surface microstructure inhomogeneities such as porosity, oxides inclusions and eutectic silicon clusters, whereas low-cycle fatigue cracks initiated from shear slips which were also influenced by DAS and porosity. Different fatigue fracture features were related to the orientation and localized stress states of the underlying dendrite microstuctures. The effects of porosity, DAS, eutectic silicon particles on the fatigue crack propagation were also investigated.

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CREEP MECHANISMS IN DIE CAST MAGNESIUM ALLOYS AZ91D AND AE42: *Keun Yong Sohn*[1]; J. Wayne Jones[1]; John E. Allison[2]; [1]University of Michigan, Dept. of Mats. Sci. and Eng., 2300 Hayward St., Ann Arbor, MI 48109 USA; [2]Ford Motor Company, Mats. Sci. Dept., Scientific Research Lab., Dearborn, MI 48121 USA

Magnesium alloys for powertrain components such as transmission case require good creep resistance at elevated temperatures. This study involves the characterization of creep of high pressure die-cast magnesium alloys, AZ91D and AE42. The effect of temperature and stress on creep behavior was investigated and correlated with cast microstructures. The creep strain rate, stress exponent and activation energy were

investigated to identify the responsible creep mechanisms for each alloy. AZ91D showed a very short range of steady state creep (better characterized as a minimum creep rate). AE42 showed a relatively long range of steady state creep, especially at lower stress levels. The stress exponent of steady state creep for AZ91D was about 5.5-6 at 150°C, while that of AE42 changed as the applied stress increased from 40 to 90 MPa. TEM investigation of crept specimens have been conducted to characterize differences in deformation mechanisms between AZ91D and AE42. Directions for the development of new creep resistant magnesium alloys will also be discussed.

5:10 PM
EFFECTS OF IRON PHASES ON THE MECHANICAL PROPERTIES OF A CAST ALUMINUM ALLOYS: *A. Rodriguez*[1]; [1]Faculted de Ingenieria Mecanica y Electricia Mexico

Automotive components require strict quality control to withstand the working conditions to which they are subjected to, Mechanical properties of aluminum alloys cast in permanent mold properties are affected by iron intermetallics, these hard and brittle phases develop during solidification and increase the possibility of developing cracks in the piece. A series of experimental trials were carried out in a type 319 alloy, content of iron was fixed at two levels: 0.3 and: 0.7% in weight. The melt was refined with a Ti-B master alloy and modified with strontium. Samples were poured in metallic and silica sand moulds, the solidification process was recorded with type K thermocouples inserted in the moulds. Thermal analysis was employed to obtain information related to the precipitation of iron phases, as well as the other reactions that take place during solidification. Mechanical tests were realized and the mechanical properties were correlated to the aspect and size of the iron phases.

CARBON TECHNOLOGY: Cathode Material & Corrosion

Sponsored by: Light Metals Division, Aluminum Committee
Program Organizer: C. Dreyer, Aluminium Pechiney, St. Jean De Maurienne 73303 France

Tuesday PM Room: 6D
March 2, 1999 Location: Convention Center

Session Chair: Daniel Dumas, Carbone Savoie, Venissieux Cedex, France

2:00 PM SESSION CHAIRMAN INTRODUCTION

2:05 PM
PRODUCTION AND PERFORMANCE ASPECTS OF RAMMING PASTE: *Raymond C. Perruchoud*[1]; Urs Buhler[1]; Werner K. Fischer[1]; [1]R&D Carbon, Ltd., P.O. Box 362, Sierre CH-3960 Switzerland

Experiences of process optimization are reviewed which have been performed in smelters producing ramming paste. For a high and consistent paste quality, a proper selection of raw materials adapted to the process capabilities of a given plant is mandatory. Different possibilities of adjusting the binder viscosity and its impact on paste ramming or rolling as well as on paste ramming performance are addressed. The requirements for paste used in modern cells is assessed. Paste plant design and equipment requirements are evaluated.

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CARBONACEOUS GLUEING PASTES: *Siegfried Wilkening*[1]; [1]VAW Aluminium Technologie GmbH, P.O. Box 2468, Bonn, D-53014 Germany

A comprehensive survey as well as a substantial number of experimental results will be presented on various binders and filler materials of glueing pastes which can be carbonised and form a high-temperature bond. Examples will be given for the application of appropriate glueing pastes in the field of cathode construction and anode suspension.

2:55 PM
EVALUATION OF THE CONTACT RESISTANCE BETWEEN RODDING MIX AND COLLECTOR BAR USING THE 1/5 SCALE OF CATHODE CARBON: Shinjiro Toda[1]; Katsumi Tayama[1]; *Tsutomu Wakasa*[1]; [1]Nippon Denkyou KK., Kambara Works, Kambara 5600, Kambara-cho, Ihara-Gun, Shizuoka Pref. 421-3203 Japan

We made a study to evaluate the contact resistance between rodding mix and collector bars. As this contact resistance is one of the important factors for cathode lining drop in aluminum reduction pots, many studies of it have been made in the past. Its measurement, however, is very difficult, particularly at the lower contact pressure which is probably generated in the actual pot. We used a 1/5 scale of cathode carbon with the rodded collector bar and made a measurement of the contact resistance from the cathode voltage drop by giving it current. Locating molten metal on the upper surface of the cathode carbon, we formed an equipotential surface similar to an actual pot and calculated the contact resistance by measuring each voltage drop at the collector bar, rodding mix and cathode carbon. We also made a rodding mix comparison using this method.

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COMPUTER SIMULATION OF THE ANTHRACITE CALCINING FURNACE: *R. T. Bui*[1]; Jean Perron[2]; Jean-François Dessureault[3]; [1]Universite Du Quebec A Chicoutimi, Chicoutimi, Quebec G7H 2B1 Canada; [2]Alcan International, Ltd., Jonquire, Quebec G7S 4K8 Canada; [3]Societe D'Electrlyse Et De Chimie Alcan Limitee, Jinquire, Quebec G7S4L2 Canada

Calcined anthracite is used in large quantity to manufacture the cathode blocks for use in the aluminium electrolytic cells. Calcination must be carried out properly to ensure a good quality of the anthracite especially in terms of low electric resistivity, and mechanical resistance at high temperature. Anthracite is calcined in cylindrical vertical electric furnaces in which the granular material flows down from top and is discharged at the bottom. Furnace control is based on the electric current passing through the furnace. Computer simulation is considerably complicated by the need to account for the heat treatment history of the anthracite. On one hand, the electric resistivity of anthracite measured at the high calcining temperature is not the same as that measured when the calcined anthracite has cooled down to lower temperature. On the other hand, a different cooling curve applies to each calcining temperature. A model is proposed that accounts for all above mechanisms. It simulates the furnace under its own control, which means that a control emulator is built into the furnace model. It is used to study furnace behaviour under different geometries (change in inter-electrode distance), perturbations (change in incoming anthracite properties), production schedules (increased or decreased production) or discharge schemes (discontinuous or continuous discharge). The model can be a useful tool for operating the furnace under changing production requirements all the while maintaining product quality.

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GRAPHITIZED CATHODES WITH INCREASED ABRASION RESISTANCE: *Frank Hiltmann*[1]; [1]SGL Carbon GmbH, Griesheim Plant, Stroofstrasse 27, Frankfurt D-65933 Germany

Cathode wear, especially with graphitized blocks, has moved and more into the center of interest in the aluminium smelting industry since the average cell life has substantially increased during the last decades. Apart from TIB2 plasma-spray coating as protective layer cathode production-scale studies were performed in order to create a harder graphitized cathode material with increased abrasion, i.e. mechanical wear, resistance. The (non-coated) specimen showed an increase of mechanical strength by up to 35%. Abrasion tests yielded a wear reduction by up to 22%. Thermal and electrical properties remained practically unaffected making such materials promising alternatives for smelters in which cathode erosion is a major pot failure or shutdown criterion.

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CARBON CATHODE CORROSION BY ALUMINIUM CARBIDE FORMATION: Xianan Liao[1]; *Harald A. Oye*[1]; [1]Norwegian University of Science and Technology, Institute of Inorganic Chemistry, Trondheim N-7034 Norway

The carbon cathode corrosion by Al4C3 formation is electrochemical in nature. The corrosion in the mixture of aluminium and a cryolitic melt without an externally applied current is galvanic; little corrosion occurs in an alumina-saturated acidic melt without short-circuit between the carbon sample (cathode) and the aluminium (anode). When an external current is applied, the corrosion is electrolytic and is one of the parallel cell reactions. Solid Al4C3 is formed electrochemically and it may subsequently dissolve chemically into the melt. Addition of Al4C3 reduces the galvanic corrosion due to its suppression of carbide dissolution and the increased resistance polarisation. In the case of electrolytic corrosion, carbide addition increases corrosion at a low current density, has little influence at an intermediate current density and reduces corrosion at a high current density.

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REDUCED AND ENHANCED SODIUM EXPANSION BY CARBON BONDED COATINGS: Xianan Liao[1]; *Harald A. Oye*[1]; [1]Norwegian University of Science and Technology, Institute of Inorganic Chemistry, Trondheim N-7034 Norway

Effects of coatings consisting of fillings Al4C3, TiC, TiB2, TiO2 or their mixtures and a carbonaceous binder on sodium expansion are investigated. In the basic alumina saturated cryolitic melt and at a current density of 0.70 A/cm2, a 180% to 600% increase in expansion was observed for the Al4C3-coated carbon samples compared to the expansion of the corresponding uncoated samples. This strong expansion enhancement is attributed to diffusion hindrance by the coating resulting in an increased sodium concentration at the cathode surface. All coatings present a certain resistance to sodium penetration and slow down the sodium expansion initially for a period of time, depending mainly on the current density employed. Additives increasing the electrical resistivity of the coating increase the sodium expansion. The TiB2 coating is best wetted by molten aluminium and considerably reduces sodium expansion.

CAST SHOP TECHNOLOGY: Molten Metal Processing/Grain Refining II

Sponsored by: Light Metals Division, Aluminum Committee
Program Organizers: Y. Sahai, The Ohio State University, Dept. of Mats. Sci. and Eng., Columbus, OH 43210-1179 USA; James O'Donnell, Commonwealth Aluminum, Dept. of Eng., Louisville, KY 40202 USA

Tuesday PM Room: 6C
March 2, 1999 Location: Convention Center

Session Chair: Dr. William C. Setzer, K.B. Alloys, Inc., Robards, KY 42452 USA

2:00 PM

AN EVALUATION OF METAL CLEANLINESS AND GRAIN REFINEMENT FOR 5182 ALUMINUM ALLOY DC CAST INGOT USING Al-3%Ti-0.15%C AND Al-3%Ti-1%B GRAIN REFINERS: *Anna J. Whitehead*[1]; Paul S. Cooper[2]; Ron W. McCarthy[3]; [1]Shieldalloy Metallurgy Corporation, Aluminum Products and Powders Division, P.O. Box 768, Newfield, NJ 08344-0768 USA; [2]London & Scandinavian Metallurgy Company, Ltd., Aluminium Division, Fullerton Rd., Rotherham, South Yorkshire S60 1DL England; [3]Reynolds Metals Company, Corporate Research and Development, 13203 N. Enon Church Rd., Chester, VA 23831-3122 USA

The Al-3%Ti-0.15%C grain refiner, which represents a new generation in grain refinement, has been used commercially for three years. Differences have been noted in melt cleanliness, ingot surface, and grain structure of the ingot cross-section when Al-3%Ti-0.15%C was substituted for Al-3%Ti-1%B. These differences have been evaluated by production scale DC ingot casting of aluminum alloy 5182 at the Reynolds Corporate R&D Cast House in Chester, VA. Ingots of aluminum alloy 5182 were produced with each grain refiner, Al-3%Ti-0.15%C and Al-3%Ti-1%B. The addition point of the grain refiner rod was varied among three locations: before the spinning degasser, between the spinning degasser and the ceramic foam filter, and after the ceramic foam filter. Molten metal cleanliness was characterized using the LiMCA II system and LAIS inclusion sampling. Comparisons were made of the grain refinement using the Aluminum Association's TP-1 Test, the ALCOA Cold Finger Test, and the etched ingot cross-sections. The effect of the grain refining nucleation particles, TiC and TiB_2, on the molten metal cleanliness and the interaction with filtration systems are described. A summary of the impact of the use of Al-3%Ti-0.15%C vs. Al-3%Ti-1%B grain refiner on commercial alloy production is discussed.

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FACTORS INFLUENCING THE EFFECTIVENESS OF THE Al-Ti-C GRAIN REFINER: *W. C. Setzer*[1]; A. Hardman[1]; G. W. Boone[1]; [1]KB Alloys, Inc., Corporate Technology, 3293 McDonald Rd., Robards, KY 42452 USA

The system Al-Ti-B has been used extensively over the past forty years for grain refining aluminum alloys and has been shown to be cost effective in providing increased casting rates without cracking and to prevent grain structure detrimental to surface appearance in a number of alloy systems. More recently, the Al-Ti-C system has been examined to determine whether it can offer specific benefits over the Al-Ti-B system. As with the Al-Ti-B system, the alloys reported on have included a number of Ti and C levels. However, there has not been an investigation which has definitively determined the relationship between grain refining effectiveness and C and Ti content for optimized processing conditions. This study was undertaken in order to examine in a systematic way the changes in grain refining effectiveness with changes in titanium content and carbon content in commercial purity aluminum containing various residual titanium levels. The discussion will include a review of these results and a literature survey, and their impact on the present view of the operative grain refining mechanism for both the Al-Ti-B and the Al-Ti-C systems.

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ALTIC GRAIN REFINERS WITH NUCLEATION POWER: *P. C. van Wiggen*[1]; J. K. Belgraver[2]; [1]KBM Master Alloys B.V., Kloosterlaan 2, TE Delfzijl 9936 The Netherlands; [2]KBM Affilips B.V., Waalkade 2, AT Oss. 5340 The Netherlands

AlTiC grain refiners form a relatively new alternative to the existing class of AlTiB type grain refiners for achieving fine equiaxed grain structures in aluminium alloys during casting and solidification. In this contribution, difference types of AlTiC master alloys are presented. Their characteristics will be evaluated and compared to the required specification criteria. The major part of the work consists of laboratory grain refinement test work and full-scale test trials essentially comparing the performance of AlTiC grain refiners relative to each other and to their AlTiB counterparts. The performance in different grain refining tests, in various alloys and using a range of test conditions will be covered. During the evaluation of the results important factors such as the Ti/C ratio in the AlTiC grain refiners and experience on the possibility of fade in the AlTiC system will be addressed.

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EXPERIMENTAL INVESTIGATIONS OF THE EFFECT OF VARIOUS ALLOYING ELEMENTS ON AS-CAST GRAIN SIZE OF WROUGHT Al-ALLOYS: *Hans Erik Vatne*[1]; Arild Håkonsen[1]; [1]Hydro Aluminium a.s., R&D Mats. Technology, P.O. Box 219, Sunndalsøra, Sunndal N-6600 Norway

The effect of typical alloying elements on as-cast grain size of wrought Al-alloys has been investigated. The experimental investigations included various additions of the elements Fe, Si, Mg, Mn, Cu, Cr and Ti as binary Al-alloys. The results demonstrated that Ti, Cr, Mg, Si

and Cu have a positive effect on grain size, while addition of Mn increases it. The effect of the individual elements corresponds well with the growth restriction they cause. Simple empirical relationships in terms of alloy addition and growth restriction have been developed. The relationships have been tested on multi-component alloy systems of typical commercial wrought alloys. The prediction power of such empirical relationships is good, but synergistic effects occur and the formation of phases between the various elements (above the solidification temperature) reduces the prediction power. Further, the effect of growth morphology on grain size was investigated by adding Ti and Si to several alloys. Addition of Ti is in this connection relevant for most product applications, as Ti is frequently added for purposes of grain refinement, while high addition of Si is relevant for foundry alloys. It appears that a transition in growth morphology takes place at high growth restriction factors, leading to coarse grain sizes. This transition is, however, very alloy dependent.

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SECONDARY DENDRITE ARM COURSENING DURING CHEMICAL GRAIN REFINEMENT IN SOME LIGHT METALS ALLOYS: *María Eugenia Noguez*[1]; Guillermo Salas[1]; Teresa Robert[1]; Gerardo Pacheco[1]; José G. Ramírez[1]; [1]Universidad Nacional de México, F. Química/ Dept. Ing. Metalúrgica, Reforma 321, San Miguel Xicalco, México City, D.F. 14490 Mexico

In certain conditions, chemical grain refinement does not promote a refining effect on secondary dendrite arm, on the contrary it tends to coarsen. This effect has already been pointed out for Al alloys by Mondolfo. This has practical implications in segregation, properties, cooling rate curves, and homogenization times which have not been enough discussed in the literature. A series of grain refined samples using different conditions have been cast, with a successful grain refinement, the dendrite coarsening has been found in an Al-5% Zn alloy refined with 0.1-0.5% Ti-B additions in sand molds and markedly in a Mg-5% Zn alloy using 0.03-0.12% hexacloroethane as grain refiner in metallic molds. Processing variables, structural parameters and properties are reported, related and discussed. A possible explanation regarding the absence of dendrite refinement when the grain does is included.

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CORRELATION BETWEEN GRAIN REFINING EFFICIENCY AND MICROSTRUCTURE IN Al-Ti-B MASTER ALLOYS: *Juan J. Del Campo*[1]; Mauro Martin[2]; Leopoldo Galan[2]; [1]Uuiversidad De Oviedo, Mats. Sci.& Eng. Metall., Escuela Ing. T. Industrial, Avda. Manuel Llaneza, 75, Gijon, Ppincipado De Asturias 33208 Spain; [2]Asturiana De Aleaciones,S.A. Aleastur, Quality Assurance Dept., Polígono de Maqua, Zeluan, Aviles, Pincipado De Asturias 33400 Spain

Al-Ti-B master alloys present different grain refining efficiencies depending upon the microstructure among other factors. A study was undertaken in order to establish a possible correlation between grain refining potency and microstructure in 3/1 and 5/1 rods produced in an industrial scale basis. The obtained results are comment considering the different grain refining theories proposed in the scientific literature.

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EFFECT OF GRAIN REFINERS ON INTERMETALLIC PHASES IN AA1XXX SIMULATED DC CASTINGS: *X. -G. Chen*[1]; [1]Alcan International, Ltd., Arvida Research and Development Center, Jonquiere, Quebec Canada

The effect of grain refiners on intermetallic phases in commercial purity alloys was investigated using a DC simulator, which has similar cooling conditions to the subsurface region of DC cast ingots. A commercial AA1xxx alloy was cast with different addition levels of AlTiB and AlTiC type grain refiners. The microstructure and related intermetallic phases were characterized by macro-etching, SEM and x-ray diffraction analysis. It was found that TiB2 and TiC promote the formation of the metastable AlmFe phase. The nucleation sites of intermetallic particles were observed and analyzed by using deep-etching and SEM techniques. The roles of TiB2 and TiC in promoting the fir-tree structure are discussed.

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THE GENERATION OF Al_m Fe IN DILUTE ALUMINIUM ALLOYS WITH DIFFERENT GRAIN REFINING ADDITIONS: M. W. Meredith[1]; A. L. Greer[1]; P. V. Evans[2]; R. G. Hamerton[2]; [1]University of Cambridge, Department of Materials Science and Metallurgy, Pembroke Street, Cambridge CB2 3QZ, UK; [2]Alcan International Limited, Banbury Laboratory, Southam Road, Banbury OX16 7SP, UK

$Al_{13}Fe_4$, Al_6Fe and Al_mFe are common intermetallics in commercial AAlXXX series Al alloys . Grain-refining additions (based on either Al-Ti-B or Al-Ti-C) are usually added to such alloys during solidification processing to aid the grain structure development. They also influence the favoured intermetallic and, hence, can affect the materials' properties. This work simulates commercial casting practices in an attempt to determine the mechanisms by which one intermetallic phase is favoured over another by the introduction of grain-refining additions. Directional solidification experiments on Al-0.3wt.%Fe-0.15wt.%Si with and without grain refiner are conducted using Bridgman apparatus. The type, amount and effectiveness of the grain-refining additions are altered and the resulting intermetallic phase selection followed. The materials are characterised using optical microscopy, scanning electron microscopy and X-ray diffraction. Al_mFe is seen to form when Al-Ti-B grain-refiner is introduced but only when the refinement is successful; reducing the effectiveness of the refiner led to Al_6Fe forming under all conditions. Al-Ti-C refiners are seen to promote Al_mFe at lower solidification velocities than when Al-Ti-B was used even though the grain structure was not as refined. These trends can be explained within existing eutectic theory, by considering growth undercooling.

CREEP BEHAVIOR OF ADVANCED MATS. FOR THE 21ST CENTURY: Engineering Aspects

Sponsored by: ASM International: Materials Science Critical Technology Sector, Flow & Fracture Committee, Structural Materials Division, Mechanical Metallurgy Committee, Materials Processing and Manufacturing Division, Powder Metallurgy Committee

Program Organizers: Rajiv S. Mishra, University of California, Dept. of Chem. Eng. & Mats. Sci., Davis, CA 95616 USA; Amiya K. Mukherjee, University of California, Dept. of Chem. Eng. & Mats. Sci., Davis, CA 95616 USA; K. Linga Murty, North Carolina State University, P.O. Box 7909, Raleigh, NC 27695-7909 USA

Tuesday PM Room: 15A
March 2, 1999 Location: Convention Center

Session Chair: K. L. Murty, North Carolina State University, Raleigh, NC 27695-7909 USA; S. W. Nam, Korea Advanced Institute of Science and Technology, Chung Nam, Korea

2:00 PM INVITED PAPER

LIFE PREDICTION OF ZIRCALOY CLADDING BASED ON ANISOTROPIC THERMAL AND RADIATION CREEP: *K. L. Murty*[1]; [1]North Carolina State University, Dept. of Nuclear Eng., Hillsborough St., Raleigh, NC 27695-7909 USA

Zircaloy is used to clad UO2 fuel in water reactors and the integrity of the tubing is important to contain the radioactive species. These thin-walled cladding tubes experience complex biaxial stresses arising from external coolant pressure, internal pressure due to released fission gases, the pellet cladding interaction following radiation exposure, axial grid forces etc. The modeling efforts become complex due to the anisotropic nature of these hcp metals which arise from preferred grain orientations resulting from thermo-mechanical treatments during fabrication. We present here the thermal creep behavior of Zircaloy tubing studied using biaxial stressing through internal pressurization superimposed with axial load. The anisotropic creep behavior is described in

terms of creep loci at constant dissipation energy while the temperature and stress variations of creep-rate and strain were evaluated using the Dorn's creep formulations relevant to dislocation climb creep that is commonly observed in pure metals. The superimposed effects of radiation are considered in terms of stress-free radiation growth and radiation creep. Recent findings on the radiation exposure on thermal creep are described along with transients in creep following sudden stress changes. This work is funded by the National Sci. Foundation grant DMR-04818.

2:25 PM INVITED PAPER

DEVELOPMENT OF DIRECTIONALLY SOLIDIFIED NiAl ALLOYS FOR AIRCRAFT ENGINE APPLICATIONS: *S. V. Raj*[1]; I. E. Locci[1]; J. D. Whittenberger[1]; [1]NASA Lewis Research Center, Mats. Division, MS 24-1, 21000 Brookpark Rd., Cleveland, OH 44135 USA

Binary nickel aluminide has several attractive thermophysical and oxidation resistant properties which make it a potential candidate for use as turbine blades and vanes in an aircraft gas turbine engine. However, it possesses poor high temperature creep and low temperature fracture resistance properties which have limited its use in these applications. One method for potentially improving these properties is through the use of directional solidification technology. This paper reviews current strategies being employed for improving the elevated temperature creep properties of NiAl alloys.

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OXIDE-DISPERSION-STRENGTHENED CHROMIUM BASED ALLOYS WITH A COMBINATION OF HIGH TEMPERATURE STRENGTH AND OXIDATION RESISTANCE: *M. Janousek*[1]; W. Köck[1]; H. P. Martinz[1]; M. Heilmaier[2]; [1]Plansee AG, Technology Centre, Reutte/Tyrol A-6600 Austria; [2]Institute of Solid State and Material Research Dresden, Institute for Metallic Mats., Dresden D-01171 Germany

New oxide dispersion strengthened chromium based alloys (chromium content > 50 weight%, trade name Ducrolloy) for structural parts in oxidising or aggressive atmospheres at high temperature have been investigated. There are two groups of chromium alloys that differ by the type of forming oxide layer: Group A, e.g. the alloy Cr-5Fe-1Y_2O_3, with chromium oxide layers and group B, e.g. Cr-44Fe-5Al-0,3Ti-0,5Y_2O_3, with alumina layers. While alloys from group A show an excellent oxidation resistance up to 1100ϒC, alloys from group B withstand temperatures of up to 1400ϒC. A high melting point between 1500 and 1900ϒC, a protective oxide layer and the particle strengthening with oxide dispersoids of typically 20-50nm diameter lead to an unique combination of high strength and oxidation resistance at temperatures far above the application temperature of conventional iron or nickel based superalloys. Hence, the extraordinary potential of these alloys is assessed with tensile and compressive creep tests under constant strain rate conditions at two different temperatures, namely 920ϒC for a comparison with the above mentioned alloy systems and 1400ϒC revealing the perspective for future applications.

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DISPERSION HARDENED PLATNIUM MATS. FOR EXTREME CONDITIONS: Bernd Fischer[1]; *Andreas Behrends*[1]; Dietmar Freund[1]; David F. Lupton[2]; Jürgen Merker[2]; [1]Fachhochschule Jena - University of Applied Science, Materials Technology, Tatzendpromenade 1b, Jena, Thüringen D-07745 Germany; [2]W.C.Heraeus GmbH, Heraeusstraße 12-14, Hanau D-63450 Germany

Materials to withstand extreme conditions are becoming increasingly necessary for developments in high technology fields. Because of its high melting point, good high-temperature strength and chemical stability the noble metal platinum is used in the high temperature range under the simultaneous influence of thermal, mechanical and chemical loadings. In spite of its high price platinum is well suited to being used in glass melting plants for highly stressed components as well as in space technology e.g. for rocket engines. These extreme conditions require materials with improved properties. The paper will report on examinations of the microstructure and properties of dispersion hardened platinum and platinum alloys. These materials are characterized by high levels of strength and low creep rates together with sufficient ductility in long term use at highest temperatures. Small zirconium and yttrium oxide particles incorporated in the matrix effect not only these properties but also a stable fine-grained structure. The excellent chemical stability of platinum against glass melts has been maintained. The dispersion hardened platinum materials have good weldability and even in the welded state show a significantly higher stress-rupture strength than pure platinum. These properties will be discussed on the basis of extensive stress-rupture strength tests on platinum materials in various conditions at temperatures between 1200ϒC and 1700ϒC, corrosion tests in glass melts, metallographic examinations, scanning electron microscopy (SEM) and chemical microanalysis (EDX, SIMS).

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TEXTURE AND DEFORMATION OF SUPERPLASTIC ALUMINUM ALLOYS: O.A. Ruano[1]; M.T. Perez-Prado[1]; G. Gonzalezx-Doncel[1]; T. R. McNelly[2]; [1]Centro Nacional de Investigaciones Metalurgicas, C.S.I.C. Avda. Gregorio del Amo 8, 28040 Madrid, Spain; [2]Department of Mechanical Engineering, 700 Dyer road, Naval Postgraduate School, Monterey, CA 93943-5146

The deformation mechanisms in fine-grained materials deformed in the superplastic range of temperatures and strain rates are not fully understood. There are at least four different viewpoints on the roles of grain boundary sliding and slip: a) deformation occurs by grain boundary sliding with slip as the accommodation mechanism; b) grain boundary sliding and slip occur simultaneously and both contribute to deformation; c) slip occurs in the initial stages of deformation, with a transition to slip-accommodated grain boundary as microstructure evolves during straining; and d) slip predominates during superplastic deformation. Here, X-ray texture analysis methods have been coupled with recently developed computer-assisted electron backscatter pattern analysis techniques to assess the operative deformation mechanisms in various superplastic aluminum alloys. Superplastic aluminum materials may be classified according to the mechanism of transformation during annealing after deformation processing. In materials that transform by a continuous recrystalliztion reaction, superplastic flow occurs by grain boundary sliding accompanied by slip, wherein intra-granular slip occurs on two slip systems. When such materials are deformed outside of the superplastic regime, slip predominates but still occurs only on two slip systems. In alloys that transform by discontinous, or primary, ecrystallization, grain boundary sliding predominates during superplastic deformation, although slip may also occur as an accommodation mechanism. During deformation under non-superplastic conditions, slip takes place on five independent slip systems.

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SOLUTE-DRAG CREEP AND TENSILE DUCTILITY IN Al ALLOYS: *Eric M. Taleff*[1]; Paul E. Krajewski[2]; [1]University of Texas, Aerospace Eng. and Eng. Mech., ASE/EM, C0600, Austin, TX 78712-1085 USA; [2]General Motors Company, Global R&D Operations, Bldg. 1-6, Box 9055, 30,500 Mound Rd., Warren, MI 48090 USA

Solute-drag creep is an important deformation mechanism at warm-working temperatures in Al alloys containing Mg. The high strain-rate-sensitivity resulting from solute-drag creep, m = 0.3, can lead to enhanced tensile ductility, an important benefit in the commercial forming of complicated shapes. Mechanical testing of commercial Al alloys 5754 and 5182 has produced tensile ductilities in excess of 100% at temperatures of 300ϒC and higher and initial strain rates of 0.01/s. Tensile ductilities of less than half those found for 5754 and 5182 were measured for commercial alloy 7150 and an experimental Al alloy containing 5 wt pct Zn, Al-5Zn. These differences in ductility result from the primary solute additions in each material, Mg in 5182 and 5754 and Zn in 7150 and Al-5Zn. Mg leads to solute-drag creep and high ductility while Zn does not. The tensile ductilities of the two commercial 5xxx-series alloys studied do not reach those observed in low-impurity, binary Al-Mg materials, which have provided tensile ductilities of up to 325%. The ductility of the commercial alloys is limited by cavitation during solute drag creep arising from Fe, Si, and Mn additions.

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MODELLING THE ANISOTROPIC PRIMARY AND SECONDARY CREEP BEHAVIOR OF SINGLE CRYSTALS AND COM-

PARISON WITH EXPERIMENTALLY OBSERVED BEHAVIOR OF VARIOUS ALLOYS: *Uwe Glatzel*[1]; [1]Metallische Werkstoffe, Friedrich-Schiller-Universitaet Jena, Loebdergraben 32, Jena D-07743 Germany

A material model is proposed which describes single crystal creep behavior by evolution equations for dislocation densities on individual slip systems. An interaction matrix determines the influence from one glide system to the other. Assuming a face centered cubic crystal, allowing deformation on octahedral glide planes and cube glide planes with a Burgers vector of the type a/2 <110>, nine independent parameters of the interaction matrix can be distinguished. A parameter check of the nine independent parameters has been carried out, showing the influence of parameters on specific orientations of the load axis. If one assumes dislocation interaction of a glide system only with itself a smooth behavior is predicted with a maximum creep rate for [001] orientation, followed by [011] and [111]. This behavior has been observed for single crystal single phase Mats., such as Ni_3(AlTiTa) and a nickel solid solution crystal. If a strong interaction is assumed, the orientation dependent creep behavior is not at all smooth, instead it shows a sharp drop in creep rates mainly in symmetric positions of the standard orientation triangle. The orientations with highest creep rates are in this case those which favor single glide. Highly symmetric orientations, such as [001], [011] and [111] have strongly decreased stationary creep rates. Single crystal Nickel based superalloys show a similar behavior.

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DENSIFICATION CHARACTERISTICS OF AMORPHOUS ZrO2-Al2O3 POWDERS: *Ashutosh Suresh Gandhi*[1]; Vikram Jayaram[1]; Atul H. Chokshi[1]; [1]Indian Institute of Science, Dept. of Metall., Sir C.V. Raman Ave., Bangalore, Karnataka 560012 India

Amorphous ZrO2 Al2O3 powders produced by spray pyrolysis have been hot pressed up to ~98% relative density at temperatures of 923K or less under uniaxial pressures up to 750 MPa. The dense amorphous pellets have been crystallized to form bulk ultrafine microstructures with grain sizes in the range 10 nm to ~300 nm, with metastable and stable phases. The pronounced ability of the amorphous phases in ZrO2-Al2O3 to densify during hot pressing at very low temperatures has been investigated through hot pressing and compressive hot deformation experiments. The results of densification studies over a range of temperatures and applied pressures have been analyzed on the basis of the deformation characteristics of the fully dense amorphous compacts. The behavior of the amorphous powders has been compared with the existing models of viscous sintering.

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CREEP BEHAVIOR OF SiC/SiC CERAMIC MATRIX COMPOSITES: *Shijie Zhu*[1]; Mineo Mizuno[2]; Jianwu Cao[2]; Yutaka Kagawa[3]; [1]University of Electro-Communications, Dept. of Mech. and Control Eng., 1-5-1 Chofugaoka, Chofu, Tokyo 182-8585 Japan; [2]Japan Fine Ceramics Center, Atsuta-ku, Nagoya, Aichi 456 Japan; [3]The University of Tokyo, Institute of Industrial Sciences, Minato-ku, Tokyo 108 Japan

The tensile creep tests of SiC fiber reinforced SiC composites at 1000-1400ϒC were conducted. For the Standard SiC/SiC composite, the apparent stress exponent and activation energy for creep increase with a decrease in stress. The threshold stress approach was used to interpret the experimental data. For the Enhanced SiC/SiC composite, the apparent stress exponents for creep at high stresses are 12-14, but become 2 at low stresses. Creep of SiC matrix is attributed to control the creep rates of the SiC/SiC composites. Creep fracture mechanism and life prediction method were also discussed.

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STRENGTH AND CREEP BEHAVIOR OF Si3N4 WITH Yb2O3 AS A SINTERING AID: *Yesha Zheng*[1]; [1]University of Aveiro, Dept. of Eng.Ceramics and Glass, Aveiro 3810 Portugal

Si3N4 is one of the most promising engineering ceramic materials because of its excellent thermomechanical properties. Recently, Yb2O3 was found to be effective as a sintering aid of Si3N4 in improving the mechanical properties, especially high-temperature strength, of the material due to the formation of crystalline phases at the grain boundary. The heavier lanthanide oxides, Yb2O3, has high melting points. Microstructures typical for in situ toughened Si3N4 or self-reinforced ceramics, i.e., were observed. All materials contained thin amorphous films separating the grains. The amorphous intergranular films along grain boundaries revealed excess ytterbium and oxygen. The thickness of the intergranular films was about 1.0 and 2.5 nm for the grain boundaries and the phase boundaries, independent of additive content and heat-treatment history. Fracture toughness was dependent upon the morphology of microstructure. The retention in room-temperature strengths displayed at 1300ϒC was 80-90%, with no evidence of inelastic deformation preceding failure. The observed increase in fracture resistance was mainly attributed to crack deflection and crack bridging mechanisms. The steady-state creep rates, at 1400ϒC inflexural mode are the lowest reported for sintered Si3N4. The creep behavior was found to be strongly dependent on residual amorphous phase viscosity as well as on the oxidation behavior of these materials. The thickness and viscosity of the amorphous intergranular films are believed to play an important role in the high-temperature mechanical properties.

FLUID-FLOW PHENOMENA IN METALS PROCESSING: Electromagnetic - Emerging Technologies

Sponsored by: Extraction & Processing Division, Process Fundamentals Committee; Jt. Extraction & Processing Division and Materials Processing and Manufacturing Division, Synthesis, Control, and Analysis in Materials Processing Committee; Light Metals Division

Program Organizers: Nagy El-Kaddah, University of Alabama, Dept. of Met. & Mats. Eng., Tuscaloosa, AL 35487-0202 USA; Stein Tore Johansen, SINTEF Materials Technology, Process Metallurgy & Ceramics, Trondheim, NTH N-7034 Norway; David G. Robertson, University of Missouri-Rolla, Dept. of Metall. Eng., Rolla, MO 65409-1460 USA; Vaughan Voller, University of Minnesota, Saint Anthony Falls Lab., Minneapolis, MN 55414-2196 USA

Tuesday PM Room: 2
March 2, 1999 Location: Convention Center

Session Chairs: Rene Moreau, Institute National Polytechnique de Grenoble, Lab. EPM-MADYLAM (UPR CNRS A 9033), F-38402 Saint Martin d'Heres, Cedex France; Peter Davidson, University of Cambridge, Dept. of Eng., Cambridge, CB2 1PZ UK

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INFLUENCES OF MAGNETIC, ELECTRIC, GRAVITATION, AND TEMPERATURE FIELDS ON ONSET OF HYDRODYNAMIC FLOWS IN LIQUID METALS: *Alexander I. Raitchenko*[1]; [1]National Ukrainian Academy of Science, Institute for Problems of Mats. Sci., 142, 3, Krzhyzhanovsky St., Kiev 252142 Ukraine

Liquid metals under action of various fields (influencing simultaneously together or separately) may be in equilibrium or convective movement states. Knowledge of conditions of equilibrium and of convection onset has theoretical importance and practical value. Named conditions depend radically, in particular, on electroconductivity and on temperature coefficient of electroconductivity of liquid metals. Factors influencing equilibrium-convection onset conditions (besides the thermal expansion in the gravitational field) include the magnetic and electric fields also. If the spatial Lorentz-force originating from the crossed electric and magnetic fields' action is directed downwards its effect strengthens the gravitational action, and value of critical Rayleigh number must decrease; opposite situation (increasing of critical Rayleigh number) should be observed in case of Lorentz-force directed upwards. The extent of such an influence is determined by dimensionless complex[2] relation of spatial Lorentz- force to hydrostatic head of fluid column with unit height in the gravitational field. It is ascertained that the competition between the electromagnetic force due to non-unifor-

mity of electroconductivity on account of its temperature dependence and the buoyancy force may have the ambiguous effect: both increase or decrease of the critical Rayleigh numbers. The effect of such a balance is measured by value of corresponding dimensionless complex which may be named magnetic-electric-thermal-resistive-buoyant (METRB) criterion (number). Influences of electromagnetic-gravitational-hydrostatic relation number and METRB number can strengthen or weaken one another; in particular case they can "annihilate" mutually, and then the critical Rayleigh numbers must be remained invariable. Liquid Mg, Zn, and Cd near their melting points have positive temperature coefficient of electroconductivity values in contrast to rest metals, thus their behavior in many situation are different than for majority other liquid metals. The proposed conception is applicable to the analysis of situations in liquid metals under combinations of various fields.

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ANALYSIS AND FINITE ELEMENT SIMULATION OF MHD FLOWS WITH AN APPLICATIONS TO LIQUID METAL PROCESSING : *A. J. Meir*[1]; P. G. Schmidt[1]; [1]Auburn University, Dept. of Mathematics, Parker Hall, Auburn, AL 36849-5310 USA

We describe and analyze a finite element method for approximating the solutions of the equations of viscous, incompressible magnetohydrodynamics posed on a bounded domain with a nonideal boundary. Our method is based on a novel formulation of the underlying partial differential equations as a system of integro-differential equations. We describe the results of some recent numerical experiments relevant to metallurgy flow phenomena.

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NUMERICAL MODELING OF ELECTROMAGNETICALLY-DRIVEN TURBULENT FLOWS USING LES METHODS: F. Felten[1]; *Yves Fautrelle*[1]; Y. Du Terrail[1]; O. Metais[2]; [1]Institut National Polytechnique de Grenoble, CNRS-EPM, ENSHMG, B.P. 95, 38402 Saint Martin d'Heres Cedex France; [2]LEGI-INPG ENSHMG, P.B. 95, 38402 Saint Martin d'Heres Cedex France

Fluid flows generated by electromagnetic stirrers have been extensively investigated. Many works have been published on the subject. In most of the previous works, one-point closure models, e.g., as k-e model, have been used. Those models yield fairly good results as for the mean velocity prediction. However, they have two main drawbacks: (i) The turbulence is not predicted accurately, (ii) Such models are not well fitted for problems where the electromagnetic force are unsteady as in the low frequency magnetic stirring. We deal with the prediction of electromagnetically-driven turbulent flows by means of a Large-Eddy-Simulation method (LES). The method stems from the Smagorinsky eddy viscosity model. The model is applied in the case of a liquid metal pool submitted to a polyphase linear electromagnetic stirrer. We investigate two cases: (i) The frequency of the magnetic field is equal to 50 Hz; in that case the effects of the pulsating part of the Lorentz forces may be neglected; (ii) The frequency of the magnetic field is low (f = 1 Hz), then the oscillating part of the electromagnetic forces is taken into account. The LES predictions agree well with the mean velocity measurements, as does the standard k-e model. However, as for the turbulent kinetic energy predictions, there is a large discrepancy between the two models. When the oscillating of the Lorentz forces is taken into account, the computations show that the fluid flow is sensitive to the unsteady part of the forces. Without any fluid flow measurements, we only compare the cases with and without an oscillating part. We find that the mean velocity amplitudes are not affected by the fluctuating component of the force. As for the turbulence parameters, the turbulent kinetic energy is also weaker than in the previous case, whilst the turbulence length scale decreases.

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MATHEMATICAL MODELING OF TURBULENCE IN AN ELECTROMAGNETICALLY-LEVITATED NICKEL DROPLET: *Livia M. Racz*[1]; Shaun R. Berry[1]; Robert W. Hyers[2]; Behrouz Abedian[1]; [1]Tufts University, Dept. of Mech. Eng., Anderson Hall 204, Medford, MA 02155 USA; [2]MIT, Mats. Sci. and Eng., 77 Massachusetts Ave., Rm. 4-033, Cambridge, MA 02139 USA

Electromagnetic levitation is a containerless technique of great interest in materials processing. The presented work represents an effort to improve the understanding and prediction of turbulent flow inside electromagnetically-levitated droplets. It is shown that the flow field in a test case, a nickel droplet levitated under microgravity conditions, is a low Reynolds number turbulent flow, i.e. in the transitional regime between laminar and turbulent. Past research efforts have used laminar, enhanced viscosity, and k-e turbulence models to describe these flows. The method used in our study is the RNG algorithm. We show that an accurate description of the turbulent eddy viscosity is critical in order to obtain realistic velocity fields, and that the turbulent eddy viscosity cannot be uniform in levitated droplets. In the RNG method there are no characteristic length or time scales associated with the flow, thus allowing such anisotropic features to be captured. We perform calculations and analyses for two cases (1) small, nondeforming, spherical droplets, and (2) deforming, oscillating droplets. In addition to flow field calculations, we simulate numerically the oscillating drop method of thermophysical property measurements, and compare calculated values of viscosity and surface tension to experimentally-determined values.

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OSCILLATORY AND ROTATIONAL INSTABILITIES IN ELECTROMAGNETIC LEVITATION: J. Priede[1]; *Gunter Gerbeth*[1]; [1]Research Center Rossendorf, Inc., P.O. Box 510119, Dresden D-01314 Germany

We consider three different mechanisms which can cause spontaneous rotation or oscillation of a levitated spherical body. The first is that due to the virtual coupling between the electric current passing through the magnetic system and the variation of position of the body. This mechanism can result in unstable mass center oscillations of a levitated solid body as well as in increasing shape oscillations of a molten sample. Another type of instabilities may occur because of the coupling between the motion and the electric currents induced in the body. This effect can cause a spontaneous rotation of the body setting in as the frequency of the alternating magnetic field exceeds certain critical threshold depending on the configuration of the field. The third mechanism is due to the finite diffusion time of the magnetic field into the body which results in a delay of the induced currents with respect to the variation of body position. This may cause unstable oscillations of the mass center as well as those of the shape of liquid sample.

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BEHAVIOUR OF THE SOLID ALLOY PARTICLES DISPERSED IN LIQUID TIN UNDER THE ELECTRIC CURRENT PASSAGE: *Alexander I. Raitchenko*[1]; Victor P. Popov[1]; Alexander V. Derevyanko[1]; [1]National Ukrainian Academy of Sciences, Institute for Problems of Mats. Sci., 142, 3, Krzhyzhanovsky St., Kiev 252142 Ukrainian

If an electric current flows along some electroconductive suspension in columnar form the solid particles are experienced thermal, mechanical, and electromagnetic influences. The objects were suspension Sn (liquid) - Ni-Cr-Mo-W alloy (solid particles). This is refractory alloy on the Ni base. The direct constant current (with density ~106 A/m2) flowed through the named suspension during 180-300 sec. At the beginning of experiments samples were ones containing particles suspend uniformly in volume. Although density of solid particles was ~9000 kg/m3, i.e. higher than that of liquid Sn (~6800 kg/m3), after end of this processing in samples was nonuniform distribution of particles in volume of samples such: concentration of solid particles in lower part was smaller than in upper part of samples, and simultaneously their concentration is increased near outer surface. Firstly, there was probably natural convection of Benard-Raileigh type which had carried solid particles upwards, and, secondly, in perpendicular directions was action of spatial Lorentz-forces directed to center. The knowledge of named phenomena can be useful for elaboration of technology of dispersed materials and development of analogues fields of materials science.

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ELECTROMAGNETIC CONTROL OF LIQUID METAL JETS: D. J. Short[1]; *P. A. Davidson*[1]; [1]University of Cambridge, Dept. of Eng., Trumpington St., Cambridge CB2 1PZ UK

In this paper we discuss an electromagnetic means of controlling high-temperature, liquid-metal jets of small diameter (5mm). Operating on the combined principles of partial magnetic levitation and magnetic field concentration via a segmented copper cylinder, this will provide a pollution free means of modulating, stabilising and positioning the jet. This paper describes the design and test of a laboratory prototype based on experiments performed with liquid tin and aluminium, as well as our numerical model of the process. We also discuss the potential applications of our device in the handling of superalloys, particularly in the context of sprayforming.

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THE CROSSED ELECTRIC AND MAGNETIC FIELDS IMPACT ON WAVE FLOWING OF LIQUID METAL LAYERS: *Alexander I. Raitchenko*[1]; [1]National Ukrainian Academy of Sci., Institute for Problems of Mats. Sci., 142, 3, Krzhyzhanovsky St., Kiev 252142 Ukraine

An electroconductive viscous liquid may flow in laminar or turbulent regime under Lorentz-force born by crossed electric current and magnetic field. When there is a starting flat layer between hard and free boundaries the spatial Lorentz-force can create a specific stationary regime of flowing: free surface will transform into wavy one, and movement in the depth will be not laminar and not turbulent, but this regime will be characterized by organized forms with indications of "rolling of long cylindrical drops". It was found that wavy regime is more advantageous energetically than laminar one. Mean thickness of wavy layer is becoming lesser with movement in the direction of Lorentz-force. Length of wave is determined by viscosity, density, surface tension, specific flow of liquid, and Lorentz-force. Limit of wavy regime is determined by most long of wave which is directly proportional to the critical value of specific flow and inversely proportional to the kinetic viscosity. The proper critical value of Reynolds number is determined by dimensionless combination containing surface tension, density, viscosity, and Lorentz-force. The named dimensionless combination in our case is some criterion substituting the known Kapitsa number for case of thin viscous liquid layers under gravity. It was shown that spreading of admixture by mechanism of wavy regime is more rapid than by common diffusion. Suggested conception can be a theoretical basis for elaboration of some specific liquid metals technologies.

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CONTROL OF THE POWDER DISPERSION IN INDUCTIVE PLASMAS BY USING A DOUBLE FLOW INJECTOR: P. Proulx[2]; *C. Trassy*[1]; [1]Laboratoire EPM-Madylam, ENSHMG, BP 95, 38402 Saint Martin d'Heres Cedex France; [2]Centre de Recherches en Technologie des Plasmas, Faculte de Genie, Sherbrooke, Quebec J1K 2R1 Canada

An inductive discharge presents, in the coil region, recirculation eddies due to the Lorentz forces, resulting in an axial backflow. Generally, this axial backflow disappears on the centerline when the central jet is strong enough to "pierce" the recirculation. However the external layer of the injection flow is skimmed by the remaining eddy, and particulates are carried to the discharge periphery. This results in treatment differences for the powder: particulates rejected to the plasma periphery are not treated. To avoid this disadvantage, it is common to introduce the injection pipe inside the discharge, so that its outlet is positioned after the recirculation eddy. The powders remain confined in the axial zone, to the expense of shortened residence time. In order to increase the efficiency of the particle trajectories, a double flow injector has been designed. It enables the particles to travel closer to the axis, while the outer schrouding gas is skimmed and passes through the electromagnetic eddies. This injector is made up of two concentric tubes. The powders are injected with the carrier gas in the inner tube. A schrouding gas, for instance pure argon, is injected in the annular space between the inner and the outer tubes. The powder is confined to the vicinity of the axis, resulting in a more homogeneous thermal treatment. Tungsten powders have been spheroidized with and without this device. Using the double flow injection, the spheroidization yield has been increased from 70% up to 95%. the design of such an injection device has been improved by modelling. A visualisation technique has been used for the experimental study. Injecting yttrium oxide into the discharge results in a colorful display of the 4000 K isotherm: the "cold" zone, below 4000, appearing as red, and the "hot" zone as blue. This visualization technique drastically simplifies the comparison between experimental and theoretical results. Furthermore, it is of great industrial interest since it is a very cheap and efficient way to obtain a picture of an important isotherm. The comparison between the numerical and experimental investigation will be presented.

GENERAL ABSTRACTS: Session 6 - General Metallurgy

Sponsored by: TMS

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Tuesday PM — Room: 12
March 2, 1999 — Location: Convention Center

Session Chairs: Benji Maruyama, WL/MLLM, Wright Lab Mats. Directorate, WPAFB, OH 45433 USA; David Senor, PNL

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AN OVERVIEW OF THE DOE-OIT ALUMINUM PROGRAM: *Sara A. Dillich*[1]; *Toni Grobstein Marechaux*[1]; [1]U.S. Dept. of Energy, EE-20, 1000 Independence Ave. S.W., Washington, D.C. 20585—0121 USA

The goal of the DOE-Office of Industrial Technologies (OIT) Aluminum Industry of the Future program is to work in partnership with the aluminum industry to develop and deploy energy-efficient, and pollution prevention technologies. The program addresses technology needs and priorities identified in the Aluminum Industry Technology Roadmap (May, 1997) and the supplementary Inert Anode Roadmap (February, 1998). The portfolio consists of industrially cost-shared and partnered research in primary aluminum processing, recycling and semi-fabrication processing. The project partnerships, goals and anticipated benefits will be described, as will the project solicitation and selection process. Future plans for the program, and the relevance of other federally-funded R&D to the Roadmap goals will also be discussed.

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OZONE CONTROL OF CASTHOUSE PROCESS COOLING WATER IN A PRIMARY ALUMINIUM SMELTER: *David Rees*[1]; Peter Dann[1]; Derek Scott[2]; Peter Miller[3]; [1]Tomago Aluminium, P.O. Box 405, Raymond Terrace, NSW 2324 Australia; [2]ANCO Australasia, 102 Derby St., Silverwater, Sydney, NSW 2119 Australia; [3]Ionics Watertec, 895 Pacific Highway, Pymble, NSW 2073 Australia

Tomago Aluminium, a 400,000 tpa primary aluminium smelter in Australia has installed Ozone for biological control of its process water. The system was designed in Australian by Ionics Watertec Engeering, whilst Anco Australasia monitors the water quality and provides the technical support for the project. The motivation was initially to reduce operating costs, however investigations indicated that there were substantial environmental benefits to be achieved by the elimination of a part of, or all of, the chemicals being used to control the system. Also the existing chemicals appeared to be losing their ability to control biological growth, in particular, the legionella bacteria. Ozone commenced in January 1998 and after a short transition has operated without chemical addition since. There appears to be no doubt that the biological control is effective, the clarity and purity of the water has improved and initial testing indicates that the corrosion rate is acceptable, although some chemical corrosion control may be introduced after further testing around the total circuit to guarantee protection.

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PROTECTION OF METALS AGAINST MICROBIOLOGICALLY INFLUENCED CORROSION USING MOLECULAR SELF-ASSEMBLIES: *Rajendra Uddhav Vaidya*[1]; Susan Brozik[2]; Darryl P. Butt[1]; Larry E. Hersman[3]; Alina Deshpande[3]; Kestas Laurinavichius[4]; [1]Los Alamos National Laboratory, Metallurgy Group, MST-6, Mail Stop G

755, Los Alamos, NM 87545 USA; [2]Los Alamos National Laboratory, NMT-6, Mail Stop G 755, Los Alamos, NM 87545 USA; [3]Los Alamos National Laboratory, Life Sciences Division, LS-7, Mail Stop M 888, Los Alamos, NM 87545 USA; [4]Russian Academy of Sciences, Institute of Anaerobic Processes, Pushchino, Moscow Region 142292 Russia

The effectiveness of a self-assembled silane coating as a corrosion inhibitor for beryllium, aluminum alloy 6061, and an alumina particle reinforced aluminum 6061 matrix composite, against microbiologically influenced corrosion (MIC) was demonstrated. Tensile tests and four-point bend tests on coated and uncoated samples were conducted to test the effectiveness of these coatings. Application of these self-assembled silane coatings to the sample surfaces was found to prevent degradation of the failure strength and displacement. In contrast, the uncoated samples exhibited a severe reduction in these mechanical properties in the presence of the aerobic and anaerobic bacteria. This study demonstrates the potential for developing fast, easy, and cost-effective MIC protection for metals using self assemblies.

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METALLOGRAPHIC PREPARATION AND QUANTITATIVE IMAGE ANALYSIS OF AUTOMOTIVE PAINT SPECIMENS: *Mathias Hoffman*[1]; William R. Creech[2]; [1]Buehler, Ltd., Lake Bluff, IL USA; [2]BMW Manufacturing Corporation, Spartanburg, SC USA

This paper focuses on the metallographic preparation of automotive paint specimens. Typically, 5 different layers make up the pain on a car part. These layers are analyzed for thickness and flaws using automated image analysis equipment. The integrity of the various layers is essential for the longevity of the overall part. Automotive paints are exposed to the natural elements and potential damage from flying debris eventually causing corrosion damage. Various tests have been established in the automotive industry to simulate the exposure of a car to the elements to improve the paint quality and process. Special techniques are used to prepare these specimens metallographically to achieve gray level differences of the various layers needed to use automatic image analysis for evaluation.

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PRODUCTION OF STEEL FOAMS: *Chanman Park*[1]; Steve R. Nutt[1]; [1]University of Southern California (USC), Dept. of Mats. Sci. and Eng., University Park, Los Angeles, CA 90089-0241 USA

Steel foams have some obvious advantages over aluminum foams, including superior mechanical strength, specific stiffness, high melting temperature, corrosion resistance, and reduced thermal conductivity. Both can be used as core materials in structures where weight efficiency or energy absorption is critical, although the technology for producing steel foams is currently undeveloped. In the present work, steel foams are produced using a PM (powder metallurgy) method that involves a foaming agent. In this method, steel powder is mixed with the granular foaming agent, and the mixture is cold-pressed. The compact is heated to the melting temperature, whereby gas is evolved from the foaming agent and the material is expanded into foam. Relative densities of 1/3-1/2 are achieved in the foams, with regular pores ranging from <0.5mm to several mm. Initial results from compression tests will be presented, along with observations of associated deformation mechanisms.

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SURFACE TREATMENT OF STEEL AND CARBON WITH OZONE FOR IMPROVED BONDING TO CONCRETE: Weiming Lu[1]; *Deborah D. L. Chung*[1]; [1]State University of New York at Buffalo, Mech. and Aerospace Eng. 608 Furnas Hall, Amherst, NY 14260 USA

Surface treatment using ozone was found to be effective for steel rebar and carbon fiber for increasing the bond strength to concrete. Steel rebar surface treatment involving ozone was more effective than those involving water immersion and sand blasting, which were in turn more effective than acetone treatment. Carbon fiber surface treatment involving ozone was more effective than those involving nitric acid, NaOH, H2O2 and acetic acid. For carbon, the effectiveness of the ozone treatment is due to the increase in surface oxygen concentration and the consequent improved wettability by water. For steel, it is due to a surface oxide layer and the consequent improved wettability. The ozone treatment increased the tensile strength, modulus and ductility of short carbon fiber reinforced cement paste, in addition to increasing the degree of fiber dispersion and reducing the drying shrinkage.

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LEACHING OF ZIRCON FOR THE REMOVAL OF URANIUM, THORIUM AND IRON: *Padmakar Ramchandra Khangaonkar*[1]; Meor Yusoff[2]; Kamarudin Hussin[1]; [1]Universiti Sains Malaysia, Perak Campus, Tronoh, Perak 31750 Malaysia; [2]Malaysian Institute of Nuclear Technology, Bangi, Kajang, Selangor 52100 Malaysia

Two samples of the mineral zircon from Malaysia were examined by leaching to achieve the removal of uranium, thorium and iron from zircon. One of the samples (containing 0.16% U, 0.08% Th and 0.22% Fe) was leached in 4M HCl at 70°C, which led to the removal of 21% of the uranium present, 26.2% of thorium and 39.8% of the iron present in the mineral. Prior thermal treatment at 600°C and grinding of the material to < 45 micron size, enabled the removal of upto 72.5%, 87.5% and 80% of the uranium, thorium and iron respectively. Leaching in 20% NaOH gave a relatively better removal of uranium but a lower degree of removal of thorium andiron. With a view to assess the relation between the leaching behaviour and the presence of amorphous zircon (metamict zircon) in the sample leached, the degree of metamictization was assessed by the crystallite size and lattice strain using X-ray methods.

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AN OVERVIEW OF THE DOE-OIT ALUMINUM AND MINING PROGRAMS: Sara A. Dillich[1]; Toni Grobstein Marechaux[1]; [1]U.S. Dept. of Energy, EE-20, 1000, Independence Ave. S.W., Washington, D.C. 20585 USA

The goal of the DOE-Office of Industrial Technologies (OIT) Industries of the Future program is to work in partnership with industry to develop and deploy energy-efficient, and pollution prevention technologies. The Aluminum program addresses technology needs and priorities identified in the Aluminum Industry Technology Roadmap (May 1997) and the supplementary Inert Anode Roadmap (February 1998). The Aluminum portfolio consists of industrially cost-shared and partnered research in primary aluminumprocessing, recycling and semi-fabrication processing. The Mining program is just getting started, with the Mining Vision document (September 1998) and plans for two solicitations in 1999. The project partnerships, goals and anticipated benefits will be described, as will the project solicitation and selection processes. Future plans for the programs, and the relevance of other federally-funded R&D to the Vision and Roadmap goals will also be discussed.

GENERAL RECYCLING OF MATERIALS: Regulations and Steel Recycling

Sponsored by: Extraction & Processing Division, Light Metals Division, Recycling Committee

Program Organizers: Ilaria Accorsi, Chrysler Corporation, Product Quality, Toledo, OH 43606 USA; Isrun Bohlinger, Technical University of Berlin, Institute of Metall. Mats., Berlin D-10623 Germany; Brajendra Mishra, Colorado School of Mines, Dept. of Metall. & Mats. Eng., Golden, CO 80401-1887 USA

Tuesday PM — Room: 1A
March 2, 1999 — Location: Convention Center

Session Chairs: Robert L. Stephens, Asarco, Inc., Technical Service, Helena, MT 52602 USA; Ilaria Accorsi, Chrysler Corporation, Toledo Machining Plant, Perrysburg, OH 43551 USA; Isrun Bohlinger, Technical University of Berlin, Institute of Metall. Mats., Berlin, D-10623 Germany

2:30 PM INTRODUCTION AND WELCOME

2:35 PM INVITED PAPER

A HYDROMETALLURGICAL WAY TO RECOVER ZINC AND LEAD FROM EAF DUST: *Carla Lupi*[1]; M. Cavallini[1]; A. Ferrone[1]; D. Pilone[1]; P. P. Milella[2]; R. Mussapi[2]; [1]Universita degli Studi di Roma "La Sapienza", Dip. ICMMPM, Via Eudossiana 18, Roma 00184 Italy; [2]ANPA, Via Vitaliano Brancati 48, Roma 00144 Italy

In 1996 the Italian Agency for Environmental Protection (ANPA) has initiated a study of the environmental impact of the industrial sector of steel produced by Electric Arc Furnace (EAF). Within the framework of this study a hydrometallurgical process to treat EAF dusts was considered and developed. In this work the lead and zinc recovery from fumes coming from carbon steel production was studied. The zinc extraction consists in acidic leaching followed by SX-EW steps. The leaching sludge containing lead sulfates was treated to obtain pure lead salt and inert solid residue. The whole process has been developed not only to obtain marketable products but also to minimize effluents by recycling the main liquid streams. The solid waste mainly containing spinels was subjected to elution tests in order to verify its compatibility with environmental regulation.Next year the proposed process will be tested in a pilot plant.

3:00 PM INVITED PAPER

CHROMIUM LOSSES DURING REMELTING OF STAINLESS STEEL SCRAP: *Saad Megahed El-Raghy*[1]; H. A. Fayed[2]; [1]Cairo University, Metall. Dept., Faculty of Engineering, Cairo Egypt; [2]Delta Steel Mills, Mostorod, Cairo Egypt

Stainless steel scrap of different grades was remelted in an induction furnace. The extent of oxidation of both carbon and chromium was followed during both the melting down and the boiling process. Decarburization was carried out utilizing either air or oxygen blowing. During the melt down, Chromium loss was dependent on the condition of the furnace and the previous melt analysis. With melts of carbon content more than 0.25%, air was as efficient as oxygen blowing for carburizing, chromium losses were minimum. Increasing temperature and lowering carbon resulted in excessive chromium losses. A general correlation between Cr and C in the melt was observed which is: log [Cr]/[C] = A - (B/T). The paper will discuss these results compared to international experience.

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THE EFFECTS OF NIOBIUM AND TITANIUM ON Tin PRECIPITATION IN Fe- ALLOYS: *Xiuqing Li*[1]; [1]University of Leeds, Dept. of Mats., Woodhouse Lane, Leeds LS2 9JT UK

The paper describes the possibility of using Sn to form intermetallic compounds with the microalloying elements Nb, Ti and Al, which are commonly present in the steelmaking process. Two series of alloys based on Fe, Sn and Al with either Nb or Ti additions were prepared by arc melting under an argon atmosphere. The microstructure of the precipitates were studied by using SEM, TEM, EDS and microprobe analysis. It was found that the level of Nb addition has an effect on the formation of Sn-rich compounds. For a small Nb additions, no Sn containing compounds were found, while in the high Nb alloy, two types of Nb-rich phases were detected: a Laves phase (Fe_2Nb, hexagonal, a=0.4830 nm and c=0.7879) containing about 1 at % Sn and a Fe_2Nb_3 phase (cubic, a=1.1261nm) which is associated with alumina and not containing tin. In contrast, no Sn containing compounds were found with Ti additions. The experimental observations were compared with thermodynamic calculations performed using MTDATA.

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RECOVERY OF TIN FROM WASTE TINPLATES: *Srecko Stopic*[1]; Ilija Blagoje Ilic[1]; [1]University of Belgrade, Faculty of Technology and Metallurgy, Dept. of Nonferrous Metall., Karnegijeva 4, P.O. Box 5303, Belgrade 11 000 Yugoslavia

Recovery of tin from tinplate and production of good-quality detinned-plate for further processing in ironworks has been the subject of interest for many years. Tinplates are mostly used for production of tin containers for food industry and consumer goods. The research carried out so far included determination of the parameters of dissolution of tin from tinplates by alkaline solutions of NaOH and electrochemical recovery of tin from the alkaline solutions. During leaching, $NaNO_3$ and methanitrobenzoic acid (MNBA) as oxidants were studied. By leaching the waste tinplate which contains 0.31% Sn with a solution of 45 g/dm^3 NaOH, 28 g/dm^3 Na_2CO_3 and 15 g/dm^3 MNBA at a temperature of 70^{o}C for 60 min, a degree of tin leaching of 97% was attained. Using MNBA acid facilitates the oxidation of Sn^{2+} into Sn^{4+}, suitable for obtaining compact but not spongy Sn cathode deposit, as it was the case earlier. Recov ery of tin by electrolysis from solutions obtained by leaching was studied to determine the effect of electrolyte composition on the quality of cathode deposit and the degree of electric current efficiency. Experimental results obtained at a laboratory level were checked on an enlarged laboratory set-up where continuous leaching of tin from waste tinplate and its electrolytic recovery from the solution obtained were carried out. The experimental set-up operated under semi-industrial conditions, and about 1500 kg of waste tinplate was processed yielding about 1160 kg of tin (99% Sn).

4:15 PM BREAK

4:30 PM INVITED PAPER

THE REGULATORY ENCOURAGEMENT OF METALS RECYCLING - VETE A OTRO PERRO CON ESE HUESO: *Larry Southwick*[1]; [1]L.M. Southwick and Associates, Process Design, Extractive Metallurgy and Chemical Engineering, 992 Marion Ave., Suite 306, Cincinnati, OH 45229 USA

Many environmental regulations, especially those related to hazardous wastes, waste minimization and pollution prevention, have as a stated goal the recovery and recycling of wastes. These include RCRA (Resource Conservation and Recovery Act for hazardous and solid wastes) promulgated in 1976, TRI (Toxic Release Inventory, or SARA Title III reporting) of 1986 and the Pollution Prevention Act of 1990. Even regulations relating to Superfund sites have on occasion appeared to encourage recovery and reuse of contaminants. However, somewhere on the road between the statues and the regulations, and especially in administering regulations, recycling has lost emphasis. In many instances, the regulations have in fact both discouraged recycling as well as hindered creation of new technologies for recovery of usable constituents. This paper will examine several examples of the above situation as it applies to recovery and recycling of metals. The activities covered include wastes generated, efforts to delist wastes from hazardous classifications, contaminated site cleanup and pollution prevention. Also addressed will be the role of the US Bureau of Mines used to play in these activities and how its demise will likely hinder rational debate and competent government evaluation of alternatives.

4:55 PM PANEL DISCUSSION

EFFECT OF REGULATIONS ON THE RECYCLING INDUSTRY: Moderator: *Larry Southwick*[1]; [1]L.M. Southwick and Associates, Process Design, Extractive Metallurgy and Chemical Engineering, 992 Marion Ave., Suite 306, Cincinnati, OH 45229 USA

This panel will involve both regulators and practitioners discussing concepts and examples of recovering and recycling metals from wastes. Included will be both hazardous and solid wastes. Topics to be discussed will cover experiences dealing with regulations, how they impact handling and logistics of the wastes, what to do with the products and with residues from processing for recycle, what regulations do the cost, feasibility and business stability of recycling, the types of technologies that can be developed in such a situation and where new developments probably cannot succeed, Covered will be how the regulations might help the recycling industry, how they might hinder it, what areas of improvement are perceived, what in fact are the objectives of the different regulations, if and where those objectives are being achieved, and what future directionsmay be, both with regulations and with technologies.

5:55 PM CLOSING REMARKS

HIGH-TEMPERATURE SUPERCONDUCTORS: SYNTHESIS, FABRICATION AND APPLICATION: Fabrication & Characterization of BSCCO Tapes

Sponsored by: 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 USA; Pradeep Haldar, Intermagnetics General Corporation, 450 Old Niskayuna Rd., Latham, NY 12110 USA; Chandra Pande, Naval Research Laboratory, Mats. Sci. & Tech. Div., Washington, D.C. 20375-5000 USA

Tuesday PM Room: 18
March 2, 1999 Location: Convention Center

Session Chairs: A. A. Polyanskii, University of Wisconsin, Applied Superconductivity Center, Madison, WI 53705 USA; Giovanni Grasso, INFM, Unita di Genova, Genova 16146 Italy

2:00 PM INVITED PAPER
DEVELOPMENTS OF Bi(2223) MULTIFILAMENTARY TAPES WITH LOW AC LOSSES: *Yibing Huang*[1]; Frank Marti[2]; Eric Walker[2]; Gregoir Witz[1]; Réne Flükiger[2]; [1]University of Geneva, Applied Physics Group, 20, Rue l'ecole de Médecine, Geneva CH-1211 Switzerland; [2]University of Geneva, DPMC, 24, Quai E-Ansermet, Geneva CH-1211 Switzerland

A significant reduction of ac losses Bi(2223) multifilamentary tapes with Ag sheaths has been achieved by using oxide (BaZrO3 and SrZrO3) barriers between filaments and by means of twisting process. Different ways to introduce oxide barriers in tapes with 19 to 95 filaments are presented. The effect of different configurations of the oxide barrier and filaments on ac losses will be discussed in detail. The deformation and twisting processes have been studied, which lead to a remarkable improvement on the homogeneity of the filaments and oxide barrier. The critical current density in the filaments varied between 10'000 and 25'000 A/cm2. The variation of the critical current density with bending strain and twisting process is shown to be similar to that of tapes without barriers. The decoupling effect can be gauged by the frequency at which loss shows a maximum in a low amplitude ac field applied perpendicular to the tape. So far, the frequency of the loss maximum, fm, in Ag sheathed tapes has been enhanced from 5 Hz (untwisted) to 116 Hz (13 mm in twist pitch length). The fabrication of long length tapes (>50 m) with oxide barrier for a prototype transmission cable demonstration cooperating with Pirelle will be reported.

2:20 PM INVITED PAPER
DAMAGE MECHANICS OF POLYCRYSTALLINE HIGH-T_c SUPERCONDUCTORS: *David O. Welch*[1]; [1]Brookhaven National Laboratory, Mats. Sci. Division, Bldg. 480, P.O. Box 5000, Upton, NY 11973-5000 USA

The formation and propagation of cracks in high-T_c superconducting composites such as powder-in-tube-processed (PIT) BSCCO 2212 and 2223 wires and thick-film $YBa_2Cu_3O_x$ coated conductors play a significant role in limiting the obtainable critical current density and the service life of these conductors. In this talk I will discuss the use of damage mechanics[1] as a theoretical framework to describe the accumulation of microcracks during processing and the irreversible strain limit for polycrystalline HTSC conductors. This framework provides a theoretical basis for the description of the role of microstructure, texture, and similar variables and suggests how experimental measurements of elastic moduli, ultrasonic wave propagation, and normal-state electrical resistivity can aid in the characterization of the state of damage. 1. J. Lamaitre and J.-L. Chaboche, Mechanics of Solid Mats., Cambridge University Press (1990). This research was supported by the U.S. Department of Energy, Division of Mats. Sciences, Office of Basic Energy Sciences under Contract No. DE-AC02-98CH10886.

2:40 PM INVITED PAPER
GRAIN BOUNDARY EFFECTS IN HIGH Tc SUPERCONDUCTORS: *K. L. Zeisler-Mashl*[1]; C. S. Pande[1]; R. A. Masumura[1]; [1]Naval Research Laboratory, Mats.. Sci. & Tech. Division, 4555 Overlook Ave., SW, Washington, DC 20375-5343 USA

A high critical current capacity is one of the most important properties needed in the newly discovered high Tc superconductors for large scale applications such as electric motors. Many factors control the critical current in these Mats.. We discuss why the low population of large angle grain boundaries and the grain alignment are most critical. Specifically, the c axis texture and a-b axis alignment seem to be most important. These results are verified by texture measurements on BSCCO tapes. Bi 2212 grain texture was determined for both c axis texture using (001) pole figures from 008 reflections and a-b axis texture using (115) pole figures. Current transport properties of these tapes were also measured and correlated with texture parameters obtained from contours of the pole figures. Crystallographic arrangement of the grains was inferred from the pole figures and was found to be consistent with a model based on global alignment of the c axis and the presence of colonies of grains differing mostly in c axis twist.

3:00 PM INVITED PAPER
EFFECT OF THE PREPARATION PARAMETERS ON GRAIN CONNECTIVITY, TEXTURE, AND PINNING PROPERTIES OF Bi(2223) TAPES: *Giovanni Grasso*[1]; Antonio S. Siri[1]; Frank Marti[2]; René L. Flukiger[2]; [1]INFM, Unità di Genova, Via Dodecaneso 33, Genova 16146 Italy; [2]Université de Genève, DPMC, 24, Quai Ernest-Ansermet, Geneve 4,1211 Switzerland

In spite of the high homogeneity that can be achieved on very long samples, Ag-sheathed Bi(2223) tapes require a further improvement of their transport properties, especially in presence of large magnetic fields. We analyzed the properties of 'state of the art' Bi(2223) tapes with self field critical current density exceeding 30'000 kA/cm2 over lengths of several meters, by various transport and magnetic techniques. From a comparison between these measurements we have individuated a domain of the H-T plane where the current density is still limited by the quality of the boundaries between adjacent grains and the polycrystalline superconductor behaves as a granular one and, on the contrary, the region where it behaves like a strongly-connected body. The temperature behavior of the intrinsic Bi(2223) current density has been also evaluated. At temperatures below 30K in zero applied field, the intragrain current density is about an order of magnitude larger than the transport current density. Finally, the effect of modifications of the heat treatment process on the pinning potential of the Bi(2223) phase will be presented.

3:20 PM BREAK

3:30 PM
CONTROLLED THERMAL PROCESSING FOR Ag-Bi2223 COMPOSITE TAPE: *Hengning Wu*[1]; Su Su Wang[1]; [1]University of Houston, Texas Center for Superconductivity, 3210 Cullen Blvd., Houston, TX 77204-5932 USA

The powder-in-tube technique has been widely used to fabricate Ag-Bi2223 composite tapes. For multi-filament Ag-Bi2223 tapes with very high critical current density, a major current limiting factor is microcracks formed during processing. A controlled thermal processing is developed to minimize the formation of the cracks, in which the temperature and oxygen partial pressure are adjusted simultaneously to maintain the phase stability of Bi2223 and alleviate the induced thermal stresses due to the mismatch of thermal expansion coefficients of silver and the superconducting phase. The phase stability of Bi2223 in the Ag-Bi2223 composite tape is investigated in a range of oxygen partial pressure and temperature to determine the proper processing parameters. The critical current densities are compared for different cases of controlled thermal processing and normal slow cooling treatments.

3:50 PM INVITED PAPER

DIRECT OBSERVATION OF PHASE FORMATION IN Ag-SHEATHED Bi,Pb(2223) MONOFILAMENTARY TAPES BY NEUTRON DIFFRACTION STUDY: *Enrico Giannini*[1]; Emilio Bellingeri[1]; Reynald Passerini[1]; Rene Flükiger[1]; [1]Université of Genève, Dépt. de Physique de la Matière Condensée, 24 quai Ernest-Ansermet, Geneva CH 1211 Switzerland

High temperature neutron diffraction measurements have been performed on Bi(2223)/Ag sheathed tapes at ILL high flux reactor in Grenoble. These tapes were submitted during the measurements to exactly the same annealing condition (Ramp rates, temperatures, times, atmosphere) as used for the preparation of high performance tapes. The especially designed experimental set up with a rotating sample older, allowed us to examine with a high precision the transformation of the precursors into the Bi(2223). Indeed the neutron diffraction measurements allowed the absolute determination of the amount of 7 different crystalline phases through the whole reaction process. In particular we found strong evidence of a partial melting at a few degrees lower than the optimal annealing temperature (838ŸC in air). These results support a nucleation and growth mechanism, thus confirming earlier results. Our measurements bring to light also the fundamental role of other cuprates mainly $(Ca,Sr)_{14}Cu_{24}O_{41}$ and Bi(2201) in the process and their behaviour under different annealing conditions. An important result based on the absolute phase quantification is that no decomposition of Bi(2223) was observed during the cooling process. The observed increase of the Bi(2212) phase upon the cooling is due to crystallisation from the remaining secondary phases. The refinement of the structure revealed that the newly formed Bi(2212) phase has different crystallographic parameters.

4:10 PM INVITED PAPER

MAGNETO OPTICAL INVESTIGATION OF MULTI-FILAMENTARY Ag/BSCCO-2223 TAPES: *A. A. Polyanskii*[1]; X. Y. Cai[1]; D. C. Larbalestier[1]; Q. Li[2]; R. Parella[2]; M. W. Rupich[2]; G. N. Riley[2]; [1]University of Wisconsin, Applied Superconductivity Center, 1500 Eng. Dr., Madison, WI 53705 USA; [2]American Superconductor Corporation, Two Technology Dr., Westborough, MA 01581 USA

The magneto-optical technique (based on the Faraday rotation in a ferrimagnetic Bi-doped garnet indicator film with in-plane anisotropy) and transport measurements were used to characterize the flux behavior in both 19 and 85 multifilamentary Ag/BSCCO-2223 tapes with very high Jc values of 54-65 kA/cm2 measured at 77K and self-field. It was found by magneto-optical imaging that magnetic flux tends to enter the tapes first perpendicular to the rolling direction. The patterns of flux penetration have a specific periodic structure which depends on residual defects arising after thermomechanical treatment, which is required to densify the BSCCO filaments after partial reaction from the 2212 to the 2223 phase. The characteristic lengths of the uncracked filaments vary from 0.2- 1.5 mm for 85 filamentary tapes to the more uniform 0.25-0.35 mm for the 19 filamentary tapes. These mechanical defects are large in scale and cause significant distortion of the current trajectories. To better understand the nature of these barriers to current flow individual filaments were extracted from BSCCO tapes and were examined by magneto-optical, transport and ultrasonic experiments. The result revealed that the Jc of individual filaments ranges from 30 kA/cm2 to at least 80 kA/cm2, a variation of more than a factor of two. This means that even for the highest Jc tapes there is still a lot of room to improve current carrying capability by eliminating the barriers to current flow.

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FABRICATION OF Ag-CLAD BI-2223 TAPES FROM COPRECIPITATED PRECURSOR POWDER: *U. Balachandran*[1]; M. Lelovic[1]; V. Selvamanickam[2]; P. Haldar[2]; [1]Argonne National Laboratory, Energy Technology Division, 9700 S. Cass Ave., Argonne, IL 60439 USA; [2]Intermagnetics General Corporation, 450 Old Niskayuna Rd., P.O. Box 461, Latham, NY 12110 USA

Ag-clad Bi-2223 tapes were fabricated with precursor powders coprecipitated from a solution containing a mixture of cations. Theprecursor powder was preconsolidated in the form of a rod and inserted into an Ag tube to prepare the billet. Drawing and rolling conditions were optimized to fabricate tapes with a uniform Ag/superconductor interface. The critical current (I_c) in these tapes was more than 30% higher than that in tapes made from billets prepared by packing loose powders. Heat-treatment conditions were optimized, and processing time was reduced by 25% from that required for tapes prepared with powders made by the conventional solid-state technique. I_c values of >40 A at 77K in self-field have been obtained in long-length tapes heat treated for <100 h. The effects of powder particle size, mechanical processing, and heat-treatment conditions in enhancing the I_c of Ag-clad Bi-2223 tapes will be discussed.

HIGH TEMPERATURE COATINGS III: Coatings for Steels

Sponsored by: Materials Processing and Manufacturing Division, Surface Engineering Committee; Jt. ASM International: Materials Science Critical Technology Sector/TMS Structural Materials Division, Corrosion and Environmental Effects Committee

Program Organizers: Janet Hampikian, Georgia Tech, School of Mats. Sci. & Eng., Atlanta, GA 30332-0245 USA; Narendra B. Dahotre, University of Tennessee Space Institute, Ctr. for Laser Applic., Tullahoma, TN 37388 USA

Tuesday PM Room: 19
March 2, 1999 Location: Convention Center

Session Chairs: Narendra B. Dahotre, University of Tennessee Space Institute, Dept. of Mats. Sci. and Eng., Tullahoma, TN 37388 USA; Alejandro Sanz, Danieli Research and Development, Dept. of Mats. Develop., Buttrio 33042 Italy

2:00 PM INVITED PAPER

MICROSTRUCTURAL ANALYSIS AND PERFORMANCE EVALUATION FOR LASER CLAD STAINLESS STEEL ON PLAIN CARBON STEEL SUBSTRATES: W. Guo[1]; *A. Kar*[1]; [1]University of Central Florida, CREOLL, P.O. Box 162700, 4000 Central Florida Blvd., Orlando, FL 32816-2700 USA

Laser materials processing can produce finer and newer microstructures than conventional methods due to its inherent rapid solidification and is applied widely in many industrial applications. Laser cladding provides a way to make high-performance coatings to upgrade the properties of the substrate such as oxidation and wear resistance. The application of stainless steel coatings on carbon steel is useful for solving nuclear power plant erosion-corrosion problems that affect the feedwater, condensate and steam system piping components. Stainless steel powders 304L and 316L were deposited onto a plain carbon steel substrate to form a layer with a high corrosion resistance. A diffusion model for rapid solidification is used to predict the type of microstructures. The theoretical calculation is in good agreement with the experimental observation of microstructures. The microstructures of the interface show a complete fusion between the cladding material and the substrate. The cladding defects are minimized by controlling the processing parameters. Oxidation resistance and hardness tests were conducted to compare the properties of the clad parts with those of the base metal. The results show that laser cladding of stainless steel can improve the corrosion resistance and hardness of the surface.

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EVALUATION OF A DUPLEX STAINLESS STEEL COATING DEPOSITED ON A CARBON STEEL BY THE TIG WELDING PROCESS: C. R. Xavier[1]; A. L. B. Baptista[1]; L. C. A. Vieira[1]; E. L. Luiz[1]; *P. R. F. Ribas*[1]; [1]Escola de Engenharia Industrial Metalzrgica de Volta Redonda, UFF, Av. dos Trabalhadores, 420, Volta Redonda, RJ 27260-740 Brazil

The application of special alloys on the surface of steel components is largely used in order to confer particular properties to the steel sur-

face. Such properties are usually required when the surfaces are subjected to critical working conditions. In addition, the adequate application of an alloy with the required properties by welding may lead to a component extra life thus reducing significantly the maintenance costs. In the present work, a medium carbon steel was coated with a duplex stainless steel applied by the tungsten inert gas (TIG) welding process. The mechanical properties in the deposited material were assessed after cold working. Metallographic analysis revealed a mixed austenite and ?-ferrite microstructure in the deposited layer, absence of microcracks, as well as a reduced thermally-affected region. Such characteristics give a good indication that the deposition of this special alloy by the TIG welding process leads to a high wear resistance, good mechanical properties, as well as high ductility and tenacity.

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ELEVATED TEMPERATURE OXIDATION PROTECTION OF CARBON STEELS BY COMBUSTION CHEMICAL VAPOR DEPOSITION: *M. R. Hendrick*[1]; S. Shanmugham[1]; H. Shao[1]; A. T. Hunt[1]; [1]Microcoating Technologies, 3901 Green Industrial Way, Chamblee, GA 30341 USA

Carbon steels make up a substantial portion of the steel produced in the United States. Their uses are numerous, from aircraft parts to automobile components to nuts and bolts. Generally, carbon steel is limited to a use temperature less than 500ŸC, after which considerable oxidation weight gain results. This paper introduces the application of protective coatings by a unique, flame-based thin film deposition process called combustion chemical vapor deposition (CCVD) to increase the use temperature of AISI 1010 and 1095 steels while also providing wet corrosion resistance. The innovative CCVD process is an open atmosphere technique that does not require a vacuum or reaction chamber. High quality films are deposited comparable to those produced by traditional CVD. Steel coupons used in these experiments were maintained at low enough temperatures during the application of oxide thin films so as to prohibit any substrate oxide formation. Tests included weight gain measurements, wet corrosion tests and adhesion analyses. Results are discussed.

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CHROMIUM NITRIDE COATINGS WITH PULSED DC MAGNETON SPUTTER DEPOSITION: *Ray Y. Lin*[1]; Jin Seok[1]; [1]University of Cincinnati, Dept. of Mats. Sci. and Eng., M.L. #12, Cincinnati, OH 45221-0012 USA

Coatings of Cr and chromium nitride on steels have been investigated with RF and pulsed DC magnetron sputter deposition at various temperatures with powers in the range of 2.19 and 8.77 W/cm2. Ultra pure argon (99.99%) with nitrogen was used as the sputtering gas. X-ray diffraction analysis and microhardness measurements have been used to characterize the coatings. It was observed that increasing the sputtering power increased the coating hardness. However, due to the residual compressive stress, hillock formation was observed for coatings at high power deposition. X-ray diffraction analysis and TEM (Transmission Electron Microscope) analysis indicated that all as-deposited films were microcrystalline in nature and exhibited a BCC (body centered cubic) Cr phase for nitrogen content in the sputtering gas below 5%. For higher nitrogen contents, Cr2N and CrN phases were both detected.

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HIGH TEMPERATURE COATING SYSTEMS FOR THE STEEL INDUSTRY: *Alejandro Sanze*[1]; [1]Danieli & Company SpA., Centro Research and Development, Via Nazionale 41, Buttrio 33042 Italy

There is a large number of steel making processes in which great demands are made on the surface behavior of several components that come to direct contact with steel under various conditions. The surface quality is measured in two different ways: a) the influence of the surface properties on the quality of the products being manufactured or b) the weight of the component replacement cost in the unit economical equation and on the plant productivity. materials in contact with solidifying Continuous Casting Machine (CCM) inner mold coatings have firmly established themselves as a means for improving the product quality and enhancing a longer mold life. New chrome-free protective coating systems are introduced at the mold level for granting environmental compliance and with improved properties. Wear represents, directly or in relation with other damaging mechanisms, the most frequent cause of machine damage. Rollers are particularly subjected to various types of aggressive operating conditions. It is necessary for rolls to resist to high thermal and mechanical stresses, wear, thermal fatigue cracking and chemical aggressions among others. Under high-load rolling contact, the operating life limiting factor of a coating may be the surface components in contact with steel products, coating may provide a solution against wear, melting damage, corrosion and fatigue. Coating selection must be carefully designed for required function. An overview on several high temperature coating applications in the steel mills will illustrate the service life and productivity enhancement of coated components. Coated elements last longer and allow a more flexible and more accurate maintenance planning. New advanced steel production methods and more rigorous operating conditions are opening the possibilities for new coating techniques and new coating Mats..

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4:00 PM INVITED PAPER

FORMATION OF HIGH CHROMIUM SURFACE ALLOYS ON 21/4Cr-1Mo AND 9Cr-1Mo STEELS USING A SINGLE STEP LASER TREATMENT FOR IMPROVING THEIR HIGH TEMPERATURE OXIDATION AND CORROSION RESISTANCE: *R. Streiff*[1]; A. S. Khanna[2]; K. Wissenbach[3]; [1]Universite de Provence, Laboratoire de Physico-Chimie des Materiaux-EA 838, Equipe de Chimie du Solide-CASE 26, Centtre Sainte-Charles-3, Place Victor Hugo, Marseille, Cedex 1331 France; [2]Indian Institute of Technology-Bombay, Corrosion Sci. and Eng., Powai, Mumbai 400 076 India; [3]Institute for Lasertechnik, Aachen Germany

Laser surface alloying is becoming an important tool in modifying the surface compositions of various relatively reactive substrates for enhancing their oxidation and corrosion resistance. In the present work, heat exchanger Mats., namely 21/4Cr-1Mo and 9Cr-1Mo Steels were modified by changing their surface chemical composition by increasing the chromium and nickel concentration. This was done by a single step laser surface alloying. A 3 kW CO_2 laser in continuous mode was used for this purpose. A 50%Ni-50%Cr powder with particle size of 22-45 μm was fed simultaneously with a feed rate of 2 gm/min, using a line focus mode with a spot size of 2 mm. Various samples were obtained by varying the scan speed from 500 mm/min to 1000 mm/min. After laser treatment the samples were characterized for surface morphology, surface composition and cross section of laser melted zone. Oxidation tests are being conducted in air at 800ŸC and aqueous corrosion tests in 1N H_2SO_4 solution and 3.5% NaCl solution. One of the aims of the work is to compare the results on the surface composition, microstructure, corrosion and oxidation with alloys of similar composition, made earlier using two step laser surface alloying.

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USE OF THE SPOTFACE TECHNIQUE TO REDUCE ASSESSING TIME OF THE PAINTED GALVANIZED STEEL UNDERFILM CORROSION: J. C. G. Carneiro[1]; A. N. C. Costa[1]; *P. R. F. Ribas*[1]; [1]Escola de Engenharia Industrial Metazrgica de Volta Redonda, UFF, Av. dos Trabalhadores, 420, Volta Redonda 27260-740 Brazil

The increasing interest of the steel industry on materials with higher corrosion resistance has led to a continuous development of the corrosion process evaluation techniques. One major goal of the new methods is to reduce the analysis time. A common technique consists in scribing the painted galvanized steel surface in order to expose steel to the corrosion environment but still demands usually long times for measurement. In this work, a new analysis technique for assessing the underfilm corrosion propagation is used with the major benefit of reducing the time of analysis, without altering the basic corrosion mechanisms. In this method, industrially-painted galvanized steel sheets have the painting and coating removed from a 13-mm diameter spot in order to increase the cathodic/anodic area ratio. This increase leads to a lower sacrificial layer protection power thus reducing significantly the total time of the corrosion test as compared to the time consumed during the scribe method test.

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CHARACTERIZATION AND TRIBOLOGICAL BEHAVIOR OF BORIDE COATING ON STEEL DEPOSITED BY LASER: Arvind Agarwal[1]; *Narendra B. Dahotre*[1]; [1]University of Tennessee Space Institute, Dept. of Mats. Sci. and Eng., Center for Laser Applications, B. H. Goethert Parkway, Tullahoma, TN 37388 USA

Titanium diboride coatings are deposited on AISI 1010 steel using a Nd:YAG laser. An ultrahard "composite" coating is produced on the steel surface comprising of titanium diboride particles and iron. The coating is adherent and metallurgy sound in nature. Microstructural characterization is performed using SEM, EDX, XRD and TEM. As a consequence of non-equilibrium synthesis by laser, formation of a novel metastable phase(s) is also indicated. Tribological characterization of the boride coatings is performed using a block-on-disc test. In addition to microhardness measurements, nanoindentation tests are also carried out for mechanical characterization of the boride coating. The work is partially supported under the subcontract from United States Air Force through Mats. Modification, Inc.

5:00 PM

ROLE OF RARE EARTH OXIDE COATINGS IN HIGH TEMPERATURE OXIDATION: *S. Seal*[1]; [1]University of Central Florida, AMPAC and MMAE, Eng. 381, P.O. Box 162450, 4000 University Blvd., Orlando, FL 32816 USA

High temperature material degradation or protection of Fe-Cr alloys and steels are often related to the nature of their oxide scale formation. Breakdown of passive films leads to localized corrosion. Many a times, various alloying elements are incorporated in these alloys to prevent high temperature degradation. Addition of alloying elements are cumbersome and not always cost effective. In this paper, we investigate the role of rare earth oxide coatings on high temperature corrosion prevention of both low and high Cr steel. An in-situ high temperature oxidation set up has been built to study the oxidation kinetics of both coated and uncoated alloys under ambient pressure and dry air. The oxide films are characterized by SEM, XPS, AES to understand the scale morphology, chemistry and structure. This work relates some of these data to explain the linear, para-linear and parabolic growth kinetics observed in both low and high Cr steels.

5:20 PM

A NEW DIFFUSION COATING RESISTIVE TO HOT SULPHURIC ACID: *Karol Jozwiak*[1]; Andrzej Mlynarczak[2]; Piotr Grzesiak[3]; Jan Jakubowski[2]; Teresa Gapinska[3]; Gerard Mesmacque[1]; [1]Universite de Lille 1, IUT A, Rue de la Recherche, Villeneuve d'Ascq, Nord Pas de Calais 59653 France; [2]Politechnika Poznanska, Instytut Inzynierii Materialowej, Pl.M.Sklodowskiej-Curie 5, Poznan, 60-965 Poland; [3]Instytut Chemii Nieorganicznej, ul. Miczurina, Poznan, 61-653 Poland

Different special steels used in sulphuric acid plants, mainly for acid coolers have been reviewed with special attention to their corrosion-resistance at elevated temperatures. Our investigations were oriented towards formation of a coating with better corrosion-resistance to hot (150-300°C) concentrated sulphuric acid. Two methods were employed: PVD by plasma jet and CVD using a mixture of powders. The coatings in the systems: C-Cr; Si-Cr; Si; B; Ni-B; Si-B; Ni-Cr were obtained on plain constructional steels with carbon content in the range of 0.1-0.5 wt%. The coatings have been characterized by optical microscopy, microhardness, SEM and EPMA and X-ray diffractometry. The corrosion tests have been performed on a laboratory scale in the temperature range of 150-250°C during 500-2000 h. The coatings are composed of intermetallic compounds and solid solutions. The outer layer is always porous so it can be concluded that the inner solid solution layer is responsible for corrosion-resistance. A coating of the type Si-B formed by CVD powder method revealed the best corrosion-resistance with corrosion rate of 0.1 mm/year compared to the Sandvik SX steel 0.6 mm/y and a type 18-9 stainless steel 1.5 mm/y.

HUME ROTHERY SYMPOSIUM TO HONOR M. HILLERT; ALLOY EFFECTS ON MIGRATING INTERFACES: Session III

Sponsored by: Jt. Electronic, Magnetic & Photonic Materials Division/Structural Materials Division, Alloy Phases Committee; ASM International: Materials Science Critical Technology Sector,Thermodynamic Activities & Phase Equilibria Committee

Program Organizers: Y. Austin Chang, University of Wisconsin, Dept. of Mats. Sci. & Eng., Madison, WI 53706-1595 USA; Ray Y. Lin, University of Cincinnati, Dept. of Mats. Sci. & Eng., Cincinnati, OH 45221-0012 USA

Tuesday PM — Room: 14A
March 2, 1999 — Location: Convention Center

Session Chairs: Gary J. Shiflet, University of Virginia, Dept. of Mats. Sci., Charlottesville, VA 22901 USA; M. Enomoto, Ibaraki University, Dept. of Mats. Sci., Hitachi, Japan 316-8511

2:00 PM INVITED PAPER

DIGM IN BICRYSTALS AND POLYCRYSTALS: *Alexander H. King*[1]; [1]State University of New York, Dept. of Mats. Sci. and Eng., Nicolls Rd., Stony Brook, NY 11794-2275 USA

Diffusion-induced grain boundary migration (DIGM) has been studied widely and a broad range of experimental tests have confirmed Hillert's theory that it originates from the coherency-strain effect. However, a number of complications still exist. In particular, there are some rather interesting differences between DIGM in polycrystals and bicrystals, including the rather puzzling observation that DIGM is almost always uni-directional in bicrystal experiments, but frequently bi-directional in polycrystals. In this talk, we consider what significant differences exist between the two cases, and we focus especially upon the effects caused by triple junctions, to see if any explanations for the observed differences can be suggested. Acknowledgment: this work is supported by the NSF, grant number DMR9530314.

2:40 PM INVITED PAPER

DRIVING FORCE FOR DISCONTINUOUS PRECIPITATION AND CHEMICALLY INDUCED INTERFACE MIGRATION: *Duk Yong Yoon*[1]; [1]Korea Advanced Institute of Science and Technology, Dept. of Mats. Sci. and Eng., 373-1 Kusungdong, Yusong-Gu, Taejon 305-701 Republic of Korea

In discontinuous precipitation and dissolution (of precipitates), solute atoms diffuse along the moving grain boundaries to and from the precipitates of usually lamellar shape. The regions either enriched with or depleted of the solute atoms are formed behind the advancing grain boundaries. Liquation can also occur discontinuously. In chemically induced interface migration, the grain boundaries and intergranular liquid films migrate, forming behind them regions either enriched with or depleted of the solute atoms which diffuse along the moving grain boundaries or liquid films either from the source or to the sink. Hillert formulated theories for the driving force of these processes based on coherency strain energy in the solute diffusion zone ahead of the moving interfaces. Critical experiments have been performed by systematically varying the coherency strain in ternary alloys and the results confirm the validity of Hillert's theory. The effects of external stress on discontinuous precipitation and of the interface curvature on the boundary migration are also consistent with the coherency strain theory. The migration direction is also determined by the asymmetry of the coherency strain energy across the boundary. The grain boundary faceting can cause zigzag boundary migration and also influence the shape of the slowly moving boundaries.

3:20 PM BREAK

3:30 PM INVITED PAPER

INTERFACE MIGRATION IN NATURAL AND ARTIFICIAL LAYERED STRUCTURES: A PARALLEL BETWEEN DISCONTINUOUS AND INTERFACE MEDIATED INSTABILITIES IN MULTILAYERS: *Yves Brechet*[1]; Leonid Kinger[1]; Gary Purdy[1]; [1]ENSEEG/INPG-Domaine Universitaire, Laboratoire de Thermodynamique et Physico-Chemie Metallurgiques, 1130 Rue de la Piscine, Saint Martin D'Heres BP 75, 38402 France

Interface migration coupled with a diffusion process at the interface occurs in many situations in physical metallurgy: eutectoid reactions, discontinuous precipitation, liquid film migration, DIGM. In this class of problems, the contribution of Mats Hillert has become classic. The present contribution will focus on discontinuous precipitation as an example of a natural layered structure, and on multilayer instability as an example of an artificial one. For both examples, we will investigate the central questions open for modelling: the macroscopic kinetics of the phenomenon, and the morphological instabilities associated with interface migration. The difference between interphases and grain boundaries will be shown to have important consequences on the pattern selection process. For discontinuous precipitation we will revisit the question of spacing selection. For multilayer instability, we will investigate the continuous front and the fingering solutions for both full miscibility of the elements (discontinuous homogeneisation) and reactive systems (discontinuous peritectic reaction).

4:10 PM INVITED PAPER

MASSIVE TRANSFORMATION GROWTH KINETICS: *J. H. Perepezko*[1]; G. Purdy[2]; [1]University of Wisconsin-Madison, Dept. of Mat. Sci. & Eng, 1509 University Ave., Madison, WI 53706 USA; [2]McMaster University, Dept. of Mat. Sci. & Eng., 1280 Main Str. W., Hamilton, Ontario L8S 4L7 Canada

During the massive transformation a parent phase crystal structure is converted into different single or dual phase product structures without any change in composition. The reaction interface is driven by the free energy change due to the crystal structure change and controlled by thermally activated boundary diffusion. Once the rate limiting nucleation step is accomplished, the high driving free energy for massive growth is reflected by a rapid transformation. Interface migration rates can exceed 1 cm/sec and can yield a departure from local interfacial equilibrium due to solute trapping. For typical massive reactions involving bcc, fcc and hcp structures, the growth kinetics can be modeled by a continuous growth mechanism, but other effects involving interface conditions and step mediated growth may be important at low driving free energies. Under the limiting growth conditions at the transition into lattice shear transformations or solute partitioning, the reaction yields product structures of metastable supersaturated solid solutions.

INTERCONNECTPACK; INTERCONNECTIONS FOR ELECTRONICS PACKAGING: Structure-Property Relationship and Reliability I

Sponsored by: Electronic, Magnetic & Photonic Materials Division,
Program Organizers: Gautam Ghosh, Northwestern University, Dept. of Mats. Sci., Evanston, IL 60208-3108 USA; Sung Kang, IBM, TJ Watson Research Center, Yorktown Heights, NY 10598 USA; Rao Mahidhara, Cypress Semiconductor Corporation, San Jose, CA 95134 USA; Ephraim Suhir, Bell Labs., Murray Hill, NJ 07974 USA

Tuesday PM — Room: 17A
March 2, 1999 — Location: Convention Center

Session Chairs: M. McCormack, Fujitsu Computer Packaging Technologies; Z. Mei, Hewlett Packard Company

2:00 PM INVITED PAPER

MICROSTRUCTURAL EVOLUTION AND RELIABILITY IN FINE-PITCH SOLDER JOINTS: *J. W. Morris*[1]; C. Gonzales[1]; M. Barney[1]; [1]University of California at Berkeley, Dept. of Mats. Sci. and Eng., Center for Advanced Mats., Lawrence Berkeley Laboratory, Berkeley, CA 94720 USA

An important active trend in microelectronics packaging is the trend toward increasingly small joint sizes. As size decreases, two potential problem intrude: unusual mechanical behavior due to a relatively coarse microstructure, and bond-line brittleness due to fine voids at the solder-substrate interface. The microstructure ordinarily very fine in the initial state because of the rapid solidification rate, but coarsens during service, changing the mechanical behavior. The void structure is also very fine in the as-solidified condition, causing brittleness at the interface. Voids coarsen during subsequent processing and service, which actually improves mechanical behavior. For both reasons, the evolution of the microstructure must be taken into account to understand and control the behavior of solder joints.

2:30 PM INVITED PAPER

STRUCTURE-PROPERTY RELATIONSHIP FOR SOLDER INTERFACES: *Jian Ku Shang*[1]; [1]University of Illinois at Urbana-Champaign, Dept. of Mats. Sci. and Eng., College Of Eng., 1304 West Green St., Urbana, IL 61801 USA

Bonding between solder alloys and metallizations is often achieved by developing metallurgy reactions at the interface. Consequently, the reliability of a solder bond strongly depends on the microstructure of the solder interface. In this presentation, recent work on microstructures and fatigue resistance of solder interfaces will be reviewed. Relationship between interfacial microstructure and property will be examined on solder interfaces prepared by systematically controlling processing conditions and by additions of select alloying elements. Fatigue resistance of the newly designed interfaces was found to depend on the type of the phase(s) present at the interface as well as the morphology of the interfacial phase. Theoretical models are presented to explain the dependence of the interfacial crack resistance on interfacial microstructure.

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EFFECT OF THERMAL CYCLES ON THE MECHANICAL STRENGTH OF QUAD FLAT PACK LEADS/Sn-3.5Ag-X(X=Bi, Cu) SOLDER JOINTS: *Yoshiharu Kariya*[1]; Yasunori Hirata[1]; Masahisa Otsuka[1]; [1]Shibaura Institute of Technology, Dept. of Mats. Sci. and Eng., Shibaura 3-9, Tokyo, Minato-ku 108-8548 Japan

Tin-silver eutectic is an attractive candidate alloy to meet requirement for demanding high temperature service environment such as automotive under-hood. The alloy has, however, a melting point con-

siderably higher than that for Sn-Pb eutectic. The melting temperature of a new Sn-Ag based solder alloy could be brought close to Sn-Pb eutectic temperature by adding a third element. It is, however, not clear to what extent the additional elements affect on mechanical reliability (i.e. fatigue properties) of eutectic Sn-Ag solder alloy. In our previous study, we clarified the effect of such third element as bismuth, copper and indium on the fatigue life of bulk Sn-3.5%Ag binary alloy. In this study, Quad Flat Pack (QFP) Leads/Sn-3.5Ag-X(X=Bi and Cu) joint were thermally cycled between 243K and 403K with a ramp rate of 1.78K/min to evaluate the effect of third element on thermal fatigue damage. Both metallographic examination and mechanical pull test were performed to evaluate thermal fatigue damage of that joint. The pull strength of QFP/Sn-3.5Ag-Bi solder joints was drastically degraded due to thermal cycles. On the other hand, the pull strength of QFP/Sn-3.5Ag-Cu solder joints slightly decreased with increasing number of cycles, though its magnitude still remains higher in comparison to bismuth containing solder joint. The behavior observed here is similar to that in bulk solder material or solder/copper joint specimen.

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DAMAGE EVOLUTION GOVERNED BY MICROCRACK NUCLEATION WITH APPLICATION TO THE FATIGUE OF 63Sn-37Pb SOLDER: *V. Stolkarts*[1]; L. M. Keer[1]; M. E. Fine[2]; B. Moran[1]; [1]Northwestern University, Dept. of Civil Eng., 2145 Sheridan Rd., Evanston, IL 60208-3109 USA; [2]Northwestern University, Dept. of Mats. Sci. and Eng., 2225 N. Campus Dr., Evanston, IL 60208 USA

This paper uses methods of statistical physics, micromechanics and applied mathematics to model damage governed by nucleation of microcracks such as often occurs in eutectic tin-lead solder. This approach derives from the understanding that the nature of such damage is stochastic due to randomness of both defect geometry and material microstructure. When the damage evolution is dominated by the nucleation of new microcracks rather than expansion of the existing ones, application of percolation theory to an array of cracks gives an estimation of the percolation threshold which is related to the microcrack density. This leads to a microstructural based model for a failure criterion and for failure prediction. The model also takes into account size effect. The model has application to cases such as Sn-Pb eutectic solder where microcracks originate at interfaces between phases and between grains and remain microcracks because of microstructural obstacles to growth.

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4:00 PM INVITED PAPER

INFLUENCE OF REFLOW PROCEDURE ON THE MICROSTRUCTURE AND STRENGTH OF 62Sn36Pb2Ag SOLDER JOINTS: Y. Fahmy[1]; Di Yang[1]; *H. Conrad*[1]; [1]North Carolina State University, Dept. of Mats. Sci. and Eng., Raleigh, NC 27695-7907 USA

The influence of burn-off time at 100°C and reflow duration at 195°C on the microstructure and strength in shear of 62Sn36Pb2Ag/Cu solder joints prepared from solder paste were determined. Regarding burn-off time, it was found that the amount of porosity in a joint and its variation from specimen-to-specimen decreased with increase in burn-off time from 0 to 5 min. Associated therewith was a decrease in the scatter and an increase in the magnitude of the maximum load in the shear test. The influence of the porosity on the mechanical response was mainly to reduce the load-bearing cross sectional area. Increase in the reflow time from 1 to 37 min gave a 20% decrease in the true maximum stress and an increase in scatter from specimen-to-specimen. EDS analysis of cross sections of the solder joints revealed a significant difference in the chemical composition from the bottom to the top elevation during reflow, Sn, Pb and Ag being higher at the top compared to bottom. Furthermore, Sn and Pb were higher in the middle compared to either the top or bottom, while the reverse was the case for Ag. The compositional differences were relatively uninfluenced by the reflow duration time. The differences in composition between the top and bottom are attributed to convection.

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EFFECTS OF THICKNESS OF Ni LAYER OVER Cu PLATE ON INTERFACIAL REACTION AND RELIABILITY: *Won Kyoung Choi*[1]; Hyuck Mo Lee[1]; [1]Korea Advanced Institute of Sci. and Technology, Dept. of Mats. Sci. and Eng., Kusong-Dong 373-1, Yusong-Gu, Taejon, Choongchungnam-Do 305-701 Korea

Sn3.5Ag and Sn3.5Ag8.5In were soldered on the various substrates of bare Cu, Ni(2§≤)/Cu, Ni(4§≤)/Cu, and bare Ni plates. The morphology and composition of the intermetallic compounds at the interface were examined using SEM and XRD. With varying the Ni thickness, various intermetallic compounds were formed, those were Cu_6Sn_5 on bare Cu, $NiSn_3$ on Ni(2§ ≤)/Cu, Ni_3Sn_2 on Ni(4§≤)/Cu and Ni_3Sn on bare Ni, and wetting behavior was different. Such phenomena seemed to be caused by the type of intermetallic compounds differently formed on each substrate. Therefore the thickness of the Ni layer which reacted with solder directly have to be considered in the prediction of interfacial reaction. After annealing for 400 hours, the growth behavior and mechanical test result of each intermetallic compound were different. It was found that the intermetallic compounds formed differently with varying the Ni layer thickness have an effect on the solder reliability.

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CREEP DEFORMATION BEHAVIOR IN Sn-3.5Ag SOLDER JOINTS USING A NOVEL MAPPING TECHNIQUE: *James P. Lucas*[1]; Alan Gibson[1]; Tom Bieler[1]; K. N. Subramanian[1]; [1]Michigan State University, Mats. Sci. and Mech., A304 Eng. Bldg., East Lansing, MI 48824 USA

Bulk solder and solder joints readily deform by creeping under the influence of both static, cyclic, and thermo-mechanical loading conditions. Deformation under creep conditions is of particular interest and importance since solder Mats., in general, function at rather high homologous temperatures. Expressed in degrees absolute, even room temperature corresponds to a temperature that is 61% of the melting temperature of Sn-3.5Ag solder. Therefore, creep conditions will always persist. To investigate creep deformation and creep mechanism of thin solder joints and bulk solder Mats., a novel mapping of deformation test technique has been developed. This technique enables quantitative measurement and qualitative assessment of micro-scale deformation in small-volume, 100-micron-thick solder joints. Deformation behavior can be assessed in highly localized regions spanning the entire solder joint. Creep deformation data at the substrate/solder interface is obtainable by the proposed technique. In this investigation, creep deformation behavior is presented for both composite (Sn-3.5Ag with in situ Cu_6Sn_5 particles) and non-composite (Sn-3.5Ag) bulk solder and solder joints. Lifetime prediction for solder joints is possible using this novel technique.

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ANALYSIS OF A CATASTROPHIC FIELD FAILURE DUE TO CONDUCTIVE ANODIC FILAMENT (CAF) FORMATION: *W. Jud Ready*[1]; B. A. Smith[1]; L. J. Turbini[1]; [1]Georgia Institute of Technology, School of Mats. Sci. and Eng., 778 Atlantic Dr., Atlanta, GA 30332-0245 USA

Conductive anodic filament (CAF) formation was first reported in 1976. This electrochemical failure mode of printed wiring boards (PWB) involves the growth of a copper-containing filament substrate along the epoxy-glass interface within the PWB. The filament is observed to grow from anode to cathode, and may form an electrical short within the PWB over time. CAF formation was ascribed to moisture up-take by the PWB substrate followed by an electrochemical reaction that created mobile copper ions. Despite the proposed reduced lifetime in electronic substrates due to CAF, field failures were not identified prior to the 1990s. The failure phenomena known as CAF poses serious long-term reliability concerns in PWBs exposed to adverse and hostile environments, especially those with closely spaced conductors. In this work, a catastrophic field failure due to CAF was analyzed. The failure occurred in a high T_g PWB used in a mixed technology product. The CAF failure occurred on an inner layer of a multi-layer board (MLB) between a via and ground plane where a potential difference of 320 V existed with 0.015 nominal spacing. The nature of the CAF was analyzed using scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS). Ion chromatography (IC) and high performance liquid chromatography (HPLC) were used to identify residue extracted from the failed boards and relate those to the hot air sodler leveling (HASL)

fluid used. Recommendations are made to aid in the prevention of field failures due to CAF formation.

INTERNATIONAL SYMPOSIUM ON ADVANCES IN TWINNING: Deformation Twinning

Sponsored by: Structural Materials Division, Physical Metallurgy Committee

Program Organizers: S. Ankem, University of Maryland, Dept. of Mats. & Nuclear Eng., College Park, MD 20742-2115 USA; Chandra Pande, Naval Research Lab, Mats. Sci. & Tech. Div., Washington, D.C. 20375-5000 USA

Tuesday PM Room: 17B
March 2, 1999 Location: Convention Center

Session Chairs: S. Mahajan, Arizona State University, Dept. of Chem., Tempe, AZ 85287-6006 USA; Aristos Christou, University of Maryland, Dept. of Mats. and Nuclear Eng., College Park, MD 20742-2115 USA

2:00 PM INVITED PAPER

FORMATION OF DEFORMATION TWINS IN METALLIC CRYSTALS: *S. Mahajan*[1]; [1]Arizona State University, Dept. of Chem., Bio and Mats. Eng., P.O. Box 876006, Tempe, AZ 85287-6006 USA

A consensus has emerged that dislocations are involved in the formation of deformation twins in metallic crystals. Several models have been proposed to rationalize the role of dislocations, and they can be broadly classified into two groups: (i) "pole mechanisms" and "ratchet" or "cross-slip" sources and (ii) conversion of slip bands into microtwins. Experimental evidence on the early stages of twinning in BCC and FCC crystals will be presented. We will argue that these observations are difficult to explain in terms of the pole models and their derivatives, but are consistent with the slip band conversion hypothesis. In addition, the influence of various metallurgy variables on twinning can be accounted for using the latter model.

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DEFORMATION TWINNING: FROM ATOMIC MODELING TO SHOCK WAVE LOADING: *Ronald W. Armstrong*[1]; Frank J. Zerilli[2]; [1]University of Maryland, Mech. Eng., Bldg. 088, Rm. 2180, Eng. Classroom Bldg., College Park, MD 20742-5035 USA; [2]Naval Surface Warfare Center, Indian Head Division, 101 Strauss Ave., Indian Head, MD 20640-5035 USA

Connection is made between deformation twinning results obtained over a wide range of testing conditions on magnesium, 1010 steel, titanium, silicon-iron and Armco iron materials. In low temperature and/or dynamic tests, micro-slip pile-up stress concentrations provide a strong, nearly athermal, Hall-Petch (H-P) stress versus inverse square root of grain diameter dependence. The high H-P microstructural stress intensity (slope value) accounts for the weak thermal dependence of the twinning stress. Twinning is followed in compression by general viscoplastic yielding by slip in the "new" twin-hardened material. In computations of cylinder impact (Taylor) test results, the hardening is attributed to effective grain size refinement that also includes a strain-accommodation-type grain volume strengthening component.

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DEFORMATION TWINNING AND SHOCK STRENGTHENING IN Cu AND Cu-Al ALLOYS: *Aashish Rohatgi*[1]; Kenneth S. Vecchio[1]; [1]University of California, San Diego, Mats. Sci. Group, Dept. of AMES, 9500 Gilman Dr., La Jolla, CA 92093 USA

FCC materials have been known to undergo deformation twinning under shock loading conditions. The propensity of deformation twinning varies inversely with the stacking fault energy of the material and varies directly with the shock pressure. The deformation twins are formed within the grains and pre-existing annealing twins and contribute to the post-shock strength of the material. The strength contribution from the deformation twins can be attributed to the apparent reduction of the grain size with the deformation twin boundaries acting as "grain boundaries" restricting the dislocation motion. In the present work, pure Cu and a series of Cu-Al alloys were shock deformed at 10 and 35 GPa. The shock-deformed materials were characterized by optical metallography, TEM, ultrasonic attenuation, microhardness and quasi-static compression tests. Each of the individual strengthening mechanisms (such as dislocations, solid solution alloying, grain boundaries, etc.) present in the materials were modeled and quantified, enabling the contribution due to deformation twin density to be evaluated.

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INFLUENCE OF STACKING FAULT ENERGY, GRAIN SIZE, AND STRESS STATE ON DEFORMATION TWINNING IN FCC POLYCRYSTALS: *Surya R. Kalidindi*[1]; [1]Drexel University, Dept. of Mats. Eng., 3141 Chesnut St., Philadelphia, PA 19104 USA

This paper investigates the microstructural variables influencing the stress required to produce deformation twins in polycrystalline face-centered cubic (FCC) metals. Classical studies on FCC single crystals have concluded that the deformation twinning stress has a parabolic dependence on the stacking fault energy of the metal. In the paper, new data is presented indicating that stacking fault energy has only an indirect effect on the twinning stress. The results indicate that the dislocation density and the homogeneous slip-length are the most relevant microstructural variables that influence directly the twinnning stress in the polycrystal. The role of the stacking fault energy was observed to be critical in building the necessary dislocation density while maintaining relatively large homogeneous slip-lengths. It was also observed that the stress state (e.g. simple compression, plane strain compression, simple shear) has an important influence on both the strain hardening rates and the microstructure evolution in the low SFE polycrystals. These results will be presented and discussed.

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TWINNING IN SINGLE CRYSTALS OF HADFIELD STEEL AND AUSTENITIC STAINLESS STEEL WITH NITROGEN: *Huseyin Sehitoglu*[1]; Yuriy I. Chumlyakov[2]; Ibrahim Karaman[1]; Ken Gall[1]; Irina V. Kireeva[2]; Elena I. Litvinova[2]; Elena G. Zaharova[2]; Natali V. Luzginova[2]; [1]University of Illinois, Mech. and Indust. Eng., 1206 W.Green St., Urbana, IL 61801 USA; [2]Siberian Physico-Technical Institute, Revolution Sq. 1, Tomsk 634050 Russia

The present study has considered the deformation of single crystals of austenitic stainless steel (Fe-18wt%Cr-16wt%Ni-10wt%Mn- and 0-0.5wt%N) and Hadfield steel (Fe-13wt%Mn-1.3wt%C). An investigation into the orientation dependence and asymmetry of the critical resolved shear stresses (CRSS), hardening modulus, and fracture behavior has been carried out. The combination of strong friction forces, due to solid solution hardening with nitrogen and carbon atoms, with a low stacking fault energy leads to the appearance of non-Schmid effects. In contrast to Schmids law, the single crystals of both materials demonstrate an orientation dependence and tension-compression asymmetry of the CRSS. The [111] crystals under tension and [001] crystals under compression are characterized as "soft". Their deformation is primarily controlled by deformation twinning. In "hard" orientations ([001] at tension and [111] at compression) deformation takes place by slip, and twinning is not observed. As the test temperature is decreased, non-Schmid effects become stronger due to the favoring of twinning at low temperatures. An activation of a few of twin systems (tension [111], compression [001]) leads to high values of the work hardening rate that is conditioned by twin-twin and twin-slip interactions. During twinning, the interstitial atomic positions transform from octahedral sites to tetrahedral sites after the displacement of the leading Shocky partial (a/6<211>). Consequently, the twins act as even stronger obstacles to dislocation motion compared to twins in a pure metal. The results of this investigation provide an experimental base for the current micromechanical models of twin-twin and twin-slip interactions. These quali-

tative understandings are necessary to derive constitutive models for the deformation of polycrystalline metals that deform by combined twinning and slip.

4:35 PM INVITED PAPER

DEFORMATION TWINNING OF SAPPHIRE (a-Al2O3): *K. Peter D. Lagerlöf*[1]; Anquin He[1]; Arthur H. Heuer[1]; [1]Case Western Reserve University, Dept. of Mats. Sci. and Eng., 109000 Euclid Ave., White Bldg., Cleveland, OH 44106-7204 USA

Deformation twinning is an important mode of deformation of sapphire (alpha-Al2O3) below its brittle to ductile transition temperature. Two twinning systems have been identified in sapphire; basal twinning (K1=(0001), eta1=<10-10), K2={10-11}, eta2=<-1012>, s=0.635) and rhombohedral twinning (K1={0-112}, eta1=<0-11>, K2={0-114}, eta2=<02-21>, s=0.202), respectively. A new simple model relating dislocation slip and deformation twinning in sapphire was recently proposed by the authors and collaborators. Newly obtained experimental evidence supporting this twinning model will be presented. In addition, a brief discussion of how the twinning model can be applied to other materials (metals, alloys and inorganic compounds) will be carried out.

INTERNATIONAL SYMPOSIUM ON GAMMA TITANIUM ALUMINIDES: TiAl Alloys: Alloying/Processing

Sponsored by: Structural Materials Division,Titanium Committee, Structural Materials Committee; ASM International: Materials Science Critical Technology Sector, Materials Synthesis & Processing,
Program Organizers: Young-Won Kim, UES, Inc., Mats. & Proc. Div., Dayton, OH 45432-1805 USA; Dennis M. Dimiduk, Wright-Patterson AFB, WL/MD, WPAFB, OH 45433 USA; Michael H. Loretto, University of Birmingham, IRC, Birmingham B15 2TT UK

Tuesday PM Room: 8
March 2, 1999 Location: Convention Center

Session Chairs: Dennis M. Dimiduk, Air Force Research, Wright-Patterson AFB, WL/MD, WPAFB, OH 45433 USA; K. A. Stevens, Air Force Research Laboratory, Mats. & Manuf. Directorate, Wright-Patterson AFB, OH 45434-7817 USA

2:00 PM INVITED PAPER

ATOM-PROBE INVESTIGATIONS OF FINE-SCALE FEATURES IN TiAl ALLOYS: *Alain Menand*[1]; [1]University of Rouen, Groupe de Métallurgie Physique - UMR CNRS 6634, Faculte des Sciences, Mont Saint Aignan, Seine Maritime 76821 France

This paper reviews the APFIM results obtained on the distribution of interstitial elements, phase transformations and the solute partitioning of additional element in TiAl-based alloys. The solubility of oxygen and carbon in the gamma phase was determined by measuring interstitial concentrations in (alpha2+gamma) two-phase alloys as well as on gamma single phase TiAl alloys. The preferential location of interstitial elements (O, C, N) in the a2 phase and their very low solubilities in gamma are explained through the existence of interstitial vacancies in a titanium rich environment. Large but fine-scale compositional variations and metastable phases observed in the lamellar structure of non equilibrium state Ti52Al48 alloys are analyzed. The partition coefficients of Cr and Nb between alpha2 and gamma phases and the influence of these elements on the phase volume fraction have been studied and the results will be analyzed in terms of the possible shape of the solubility lobes in isothermal sections of ternary phase diagrams. Tomographic Atom Probe 3D images exhibiting chromium segregation both at alpha2/gamma and gamma /gamma interfaces will be presented for a GE type alloy heat treated at 1000ϒC.

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THEORETICAL AND EXPERIMENTAL STUDY OF THE SOLUBILITY OF OXYGEN IN GAMMA-TiAl AND RELATED PHASES: *Gilles Hug*[1]; Evelyne Fries[1]; [1]ONERA-CNRS, LEM, UMR 104, BP72, Chatillon 92322 France

Oxygen and other light elements (C, N) exhibit a very low solubility in the γ-TiAl phase whereas considerable amount of them can be solved in the α_2-Ti_3Al phase. From ab-initio total energy calculations we explain such difference in solubility by the chemical environment of the octahedral cavities in which oxygen sits. In short, oxygen is found to have the highest solubility in the octaedra with eight titanium atoms at summits which are present in α_2-Ti_3Al and do not exist in gamma-TiAl. This result is in contrast with the highest affinity of oxygen with aluminium than with titanium and will be discussed together with experimental results. It is also shown that oxygen can be stabilized in cavities with 3 titanium and 3 aluminium atoms in the H-phase. Alloys with different amount of oxygen have been prepared and studied by transmission electron microscopy and electron energy loss spectroscopy to assess the local atomic environement of oxygen.

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ISOTHERMAL AND CONTINUOUS COOLING DECOMPOSITION OF ALPHA AND BETA PHASES IN GAMMA TITANIUM ALUMINIDES: *Dennis M. Dimiduk*[1]; Vijay K. Vasudevan[2]; [1]Air Force Research Laboratory, Mats. & Manufact. Directorate, AFRL/MLLM Bldg. 655, 2230 Tenth St., Wright-Patterson AFB, OH 45433-7817 USA; [2]University of Cincinnati, Dept. of Mats. Sci. & Eng., Cincinnati, OH 45221-0012 USA

The last decade led to significant engineering advances and component demonstrations for gamma-alloy products. The variety of alloy chemistries and process variations available for these products results in a spectrum of microstructures and property variation for the alloys. However, the quantitative aspects of solid-state reactions and microstructural evolution kinetics, as well as the influences of alloy composition upon these, are relatively unstudied. This presentation succinctly describes the isothermal and continuous-cooling transformations for gamma alloys across a range of compositions from binary and ternary bases, to complex multicomponent chemistries of commercial interest. Time-temperature-transformation curves are compared, and the effects of Al concentration and selected alloying additions are highlighted. Aspects of producing fine-grained fully-lamellar microstructures, having controlled lamellar characteristics, in wrought mill products are discussed. Both B2-phase forming elements (Cr, Mo & W) and boron in the alloys are examined as grain-size controlling agents. When such agents are used, the lamellar transformation kinetics may be significantly altered relative to other gamma alloys, thus changing the thermal process path and affecting the perfection of the lamellar microstructures. These lead to concomitant changes in alloy properties. The prospects for attaining such structures and properties in large product scales are discussed.

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ON THE RELATION BETWEEN COOLING RATE AND SOLIDIFICATION MICROSTRUCTURE IN AS-CAST TITANIUM ALUMINIDES: *Marc De Graef*[1]; Nicholas E. Biery[1]; Linda Rishel[1]; Tresa M. Pollock[1]; Alan Cramb[1]; [1]Carnegie Mellon, Dept. of Mats. Sci. and Eng., 5000 Forbes Ave., Pittsburgh, PA 15213-3890 USA

The texture of near-gamma titanium-aluminum alloys depends in a rather sensitive way on the details of the solidification process. It has been reported that for aluminum levels below about 48 at%, the alpha phase predominantly grows with a c-axis [00.1] primary dendrite direction. For higher aluminum levels, the basal plane [10.0] type directions are the primary growth directions. For a given aluminum level, faster cooling rates correspond to c-axis growth, and slow rates are consistent with [10.0] growth. The alpha phase solidification texture is retained during subsequent phase transformations, and has a significant influence on the mechanical properties and microstructure of the as-cast material. We will report on detailed orientation imaging microscopy experiments on binary alloys with varying aluminum level, and on 48-2-2 type alloys, all in the as-cast condition. The solidification texture will be

correlated to the aluminum level and the cooling rate. This research was funded by AFOSR grant # F49620-95-1-0359.

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PROCESSING OF GAMMA-TiAl BASED ALLOYS ON AN INDUSTRIAL SCALE: *Helmut Clemens*[1]; Nico Eberhardt[2]; Heinrich Kestler[3]; [1]Universität Stuttgart, Institut für Metallkunde, Seestrasse 71, Stuttgart D-70174 Germany; [2]Montanuniversität Leoben, Institut für Metallkunde und Werkstoffprüfung, Franz-Josef-Strasse 18, Leoben, Styria A-8700 Austria; [3]Plansee AG, Technology Center, Planseestrasse, Reutte, Tyrol A-6600 Austria

This paper describes our present status in thermomechanical and near-net shape processing of gamma-TiAl based alloys on an industrial scale. The progress achieved in forging of large ingots, rolling of sheets from forged ingot as well as HIPed powders, single and multistep extrusion of ingots and HIPing of prealloyed powders to near-net shapes parts will be presented. The impact of the different prematerial routes on process economy and quality of semi-finished products will be discussed. The mechanical properties of sheets, extruded rods and HIPed powder compacts in as-processed condition and after subsequent heat-treatments will be compared. The problems which arise when heat-treatments are transferred from small lab furnaces to large industrial furnaces will be outlined. For further manufacture of semi-finished products to final TiAl components secondary processing steps are required. Examples for forming, maching and joining will be given. Finally, gamma-TiAl components based on sheet, rod or HIPed powder are shown.

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MICROSTRUCTURAL STUDIES ON DIRECT LASER FABRICATED TiAl: *Dinesh Srivastava*[1]; Issac T. H. Chang[1]; *Mike H. Loretto*[1]; [1]The University of Birmingham, IRC in Mats. for High Performance Applications, Edgbaston, Birmingham, West Midlands B15 2TT UK

Samples of Ti48Al2Mn2Nb alloy material have been atomised using the cold wall melting facility in the IRC and these powder has been used as feedstock for laser fabrication of samples. This laser treated material has been examined using optical, analytical scanning and transmission electron microscopy, both immediately after laser fabrication and after a range of heat treatments. The microstructural observations will be presented for a number of experimental conditions including powder sizes used, laser power, laser scan rate, powder feed rate and other processing parameters. The microstructure of laser treated material has been compared with the microstructures of conventionally processed material. The stability of the microstructure has been examined after different annealing treatment.

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PROCESSING OF GAMMA-TiAl BASED INGOTS AND THEIR CHARACTERIZATION: *Volker Güther*[1]; Andreas Otto[1]; Heinrich Kestler[2]; Nico Eberhardt[3]; Helmut Clemens[4]; [1]GfE Metalle und Materialien GmbH, R&D, Höfener Strasse 45, Nürnberg D-90431 Germany; [2]Plansee AG, Technology Center, Plansee Strasse, Reutte, Tyrol A-6600 Austria; [3]Montanuniversität, Institut für Metallkunde und Werkstoffprüfung, Franz-Josef-Strasse 18, Leoben, Styria A-8700 Austria; [4]Universität Stuttgart, Institut für Metallkunde, Seestrasse 71, Stuttgart D-70174 Germany

As a consequence of the progress in processing of gamma-TiAl based alloys to semi-finished products the availability of industrial-scale ingots with a defined homogeneous element distribution is strongly required. This paper describes the processing of ingots by means of vacuum arc melting. Due to the use of optimized master alloys segregation effects can be prevented and, therefore, a deviation of the Al-content of only +/- 0.5 atomic percent is achieved over the entire ingot. This high homogeneous distribution also applies for other alloying elements, e.g. Cr, Nb, Ta, Mo, Si, B, etc. The reliability of the process is demonstrated for a Ti-47Al-4(Cr,Nb,Mo,B) alloy. The characterization comprises the local distribution of chemical composition and microstructural investigations by light optical- and scanning electron microscopy. From the obtained results it is expected that cost-intensive annealing treatments prior to subsequent processing can be omitted.

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LASER FORMING OF GAMMA TITANIUM ALUMINIDE: *John H. Moll*[1]; Eric J. Whitney[2]; C. Fred Yolton[1]; Ulrike Habel[1]; [1]Crucible Materials Corporation, Crucible Research, 6003 Campsbell Run Rd., Pittsburgh, PA 15205-1022 USA; [2]The Pennsylvania State University, Applied Research Laboratory, P.O. Box 30, State College, PA 16804-0030 USA

Laser forming is a process for producing a part directly from a three dimensional computer model. The attraction of the process is that it requires no hard tooling. As a result, there is the possibility for saving considerable time and cost in prototyping or manufacturing a metal article. In the process, a laser is used to melt input powder one layer at a time; the part is built up layer upon layer. The computer model is used to index the laser and/or the part. Development of the process for conventional titanium, such as Ti-6Al-4V, is well underway with at least one commercial facility in operation. The properties of laser formed conventional titanium alloys are equal to HIP castings. Application of laser processing to titanium aluminide should be beneficial in reducing segregation, refining the microstructure and reducing lead time for hardware. This paper will describe the results of initial studies to evaluate the feasibility of applying laser forming to the manufacture of gamma titanium aluminide hardware. The process will be described in detail and the results of microstructrural and mechanical property evaluations will be presented. Comparisons will be made with cast, ingot metallurgy and powder metallurgy processes.

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MICROSTRUCTURE, POROSITY AND MECHANICAL PROPERTIES OF SPRAY FORMED GAMMA TITANIUM ALUMINIDES: *Rainer Gerling*[1]; Kaiwen Liu[1]; Peter Schimansky[1]; [1]GKSS-Forschungszentrum, Max-Planck-Strasse, 21502 Geesthacht, Schleswig-Holstein Germany

Spray forming is a powder metallurgy technology which combines the powder production and compaction process. The ideal result of spray forming is a deposit with a fine microstructure, a high degree of chemical homogeneity and a low porosity, which can be used for further processing as extrusion, forging or rolling. Using the atomization technology EIGA (Electrode Induction Melting Gas Atomization) and a specially designed collector system, spray forming experiments have been conducted. For different - binary and advanced - gamma TiAl-alloys variations of process parameters as melt flow rate, atomization gas pressure and collector drive resulted in a number of deposits of cylindrical shape. For the different alloys the results from tensile tests at room temperature are correlated to the respective porosity levels and microstructures.

INTERNATIONAL SYMPOSIUM ON GAMMA TITANIUM ALUMINIDES: TiAl Alloys: Poster Session II – 6:00 to 10:00 PM

Sponsored by: Structural Materials Division,Titanium Committee, Structural Materials Committee; ASM International: Materials Science Critical Technology Sector, Materials Synthesis & Processing,
Program Organizers: Young-Won Kim, UES, Inc., Mats. & Proc. Div., Dayton, OH 45432-1805 USA; Dennis M. Dimiduk, Wright-Patterson AFB, WL/MD, WPAFB, OH 45433 USA; Michael H. Loretto, University of Birmingham, IRC, Birmingham B15 2TT UK

Tuesday PM
March 2, 1999

Room: San Diego Ballroom A&B
Location: Marriott, North Tower

Session Chairs: Sun-Keun Hwang, Inha University, Inchon 160 Korea; Kevin J. Hemker, Dept. of Mechanical Engineering, Johns Hopkins University, 3400 N. Charles St., Baltimore, MD 21218-2686 USA; Ian J. Perrin, ALSTOM, Mech. Eng. Center, Whetstone, Leicester LE8 6LH UK

A DESCRIPTION OF THE DISLOCATION POPULATION BEHAVIOUR IN TITANIUM ALUMINIDES WITH AN ACCOUNT OF THE DISLOCATION SOURCES OPERATION: *Bella Aleksandrovna Greenberg*[1]; Michael Alekseevich Ivanov[2]; [1]Institute of Metal Physics, Ural Branch of Russian Academy of Sciences, 18 S.Kovalevskaya St., Ekaterinburg GSP-170, Sverdlovsk Region 620219 Russia; [2]Institute of Metal Physics, National Academy of Sciences, 36 Vernadsky Av., Kiev Region 252142 Ukraine

A new approach to the description of the plastic deformation processes has been developed. The dislocation ensemble is examined as a certain population, an evolution of which is defined by a multiplication of dislocations as well as their transformations, such processes occuring on the background of elastic stress fields created by the dislocation ensemble itself. The non-linear equation for the change of dislocation density with time due to the operation of sources is proposed. It is analogous to the well-known equation for the population growth, but it contains specific values, such as critical stress and characteristic time required to switch-on the dislocation sources. It is with this last value that is connected the possibility of a fast or slow mutual adjustment of the dislocation density and external stress. On this basis, an explanation was proposed for the non-monotonous stress-strain dependence observed in certain cases at the transition from elastic to plastic deformation. An analysis of the defor mation curves at various values of the systems parameters was performed with an account of the dislocation transformations in titanium aluminides. The peculiarities of plastic deformation for TiAl, Ti3Al and their lamellar structure alloys are described.

PROPERTY/STRUCTURE RELATIONSHIPS IN EXTRUDED HIGH STRENGTH TiAl-BASED ALLOYS: *D. N. Horspool*[1]; T. T. Cheng[1]; P. A. Blenkinsop[1]; M. H. Loretto[1]; [1]The University of Bimingham, IRC in Materials for high Performance Applications, Edgbaston B15 2TT UK

Current g-TiAl alloys are based on Ti-44/48 Al (at.%) with additions of a few percent of various elements. Recent work has shown that a higher percentage of alloying additions, particularly of Nb, Zr and Hf, produces alloys with superior properties. A dispersion of TiB2 particles has been shown to have a beneficial effect on the as-cast grain size of current alloys, and extrusion at temperatures around the alpha transus has been shown to develop microstructures which are on a much finer scale than those formed by forging. Three alloys containing >3 at.% of refractory alloying additions and a few percent of B and Si were plasma melted to produce 50kg ingots, which were then extruded in full section at 1200ϒC. This paper describes a preliminary assessment of the microstructures and mechanical behaviour of these three alloys, in the as-extruded and heat-treated state. A comparison is also made of the properties of these alloys after they have undergone different processing routes.

ON THE BRITTLE-DUCTILE TRANSITION OF POLYSYNTHETICALLY TWINNED CRYSTALS OF TiAl: *Dongliang Lin*[1]; [1]Shanghai Jiao Tong University, Institue of Matls. Sci. & Eng., 1954 Huashan Rd., Shanghai 200030 P.R. China

Both single-phase and two-phase TiAl alloys have the brittle-ductile transition (BDT) behavior. For polysynthetically twinned (PST) crystals of TiAl, the transition temperature is in the range of 400-600°C. However, this behavior has not been fully understood yet. In this paper, the dislocation configurations in the PST crystals deformed at room temperature and at elevated temperature have been investigated by transmission electron microscope. It was found that 1/2<112] superlattice dislocations, as an independent slip vector, can be activated easily and played an important role in the deformation. Its core structure underwent a noticeable change from sessile to gilssile in the BDT temperature range. Taking into account the behavior of the other types of dislocations, it is reasonable to ascribe the main cause for the BDT phenomenon of PST TiAl crystals to the behaviour of 1/2<112] superlattice dislocations at elevated temperatures.

THE EFFECT OF TERNARY ELEMENTS, SURFACE TREATMENT AND COATINGS OF OXIDATION OF TiAl BASED ALLOYS: *Fuhui Wang*[1]; Zhaolin Tang[1]; [1]Chinese Academy of Sciences, Institute of Corrosion and Protection of Metals, State Key Lab for Corrosion and Protection, 62 Wencui Rd., Shenyang 110015 China

The status of intermetallics as structural materials was reviewed at First International Symposium on Structural Intermetallics(ISSI-1) held at Seven Mountain Resort, Champion, Pennsylvania, 1993. Since then, many research papers have been published about the following five classes of intermetallics: a2-Ti3Al, g-TiAl, Ti2AlNb(Orthorhombic), g*-Ni3Al and b-NiAl. However, as Williams[1] pointed out in his Keynote Address at ISSI-2, 1997, There are two systems that appear to be the front runners: g-TiAl and g*-Ni3Al. g-TiAl is attractive because of its low density, which leads to good specific stiffness and strength. In the last decade, g-TiAl based alloys have been attempted to use as compressor vanes for aero-engine[2] and turbochargers for automobile[3,4]. However, the oxidation resistance of g-TiAl based alloys could mot meet the demand of the real applications, since the Al2O3 and TiO2 mixed oxide scales formed on the alloy surfaces, but not the pure Al2O3[5-7]. In the last few years, as a result of this, o xidation and protection of g-TiAl alloys have become a world-wide subject of high temperature field. In this paper, the oxidation mechanisms of g-TiAl alloys and the effects of third element additions, surface treatment and coatings on oxidation resistance of g-TiAl were reviewed. A proper coating system and applicable surface treatment technique for the protection of g-TiAl alloys were proposed,

BONDING MECHANISMS IN TERNARY Γ-TiAl+X (X = Cr, Mn, Nb): A COMPARISON BETWEEN ABSORPTION NEAR EDGE FINE STRUCTURES AND THEORETICAL PREDICTIONS: Thierry Sikora[1]; Michel Jaouen[2]; *Gilles Hug*[1]; [1]ONERA-CNRS, Lem, UMR 104, BP72, Chatillon 92320 France; [2]University of Poitiers, LMP, UMR 6630 du CNRS, Bd 3 - Téléport 2 - BP 179 - SP2MI, Futuroscope 86960 France

The electronic structure of titanium aluminides seems to play a critical role on their plastic properties by influencing the core structure of dislocations, the planar faults energies, or the Peierls relief. The addition of small quantities of a third element (Cr, Mn, Nb) modify the interatomic bonds and enhances ductility in some cases. In this work, the local atomic order and the electronic structure of γ-$(Ti_{46}Al_{54})_{97}X_3$ (X=Mn,Nb,Cr) alloys have been studied by Electron Energy Loss and X-ray absorption spectroscopies. The local crystallographic structure and the substitution sites of addition elements have been determined by EXAFS in the framework of a multiple scattering formalism. It is shown that a strong elastic relaxation exists around the solute atom. A good match between experimental near-edge structures and theoretical unoccupied states has confirmed the existence of strong Ti-d~Ti-d and Ti-

d~Al-sp hybridizations in TiAl. From a band structure formalism, the influence of the ternary solute atom on charge density distribution has been studied and has shown that they improve the intensity of the d-d bond within the (001) planes.

HOW STABLE IS THE W PHASE IN TiAl-X ALLOYS: *Guosheng Shao*[1]; Panos Tsakiropoulos[1]; [1]University of Surrey, School of Mech. and Mats .Eng., Guildford, Surrey GU2 5XH UK

This work contributes to the stability of the w phase in TiAl-X alloys by combining electron microscopy and theoretical calculations of lattice stability. Starting from experimental observations, a hypothesis on the effects of the interaction between Al and transition metal elements on the w phase stability was proposed. While the hypothesis was supported by calculated heats of formation of the w phase using the total energy LMTO method, the LMTO calculations have also given predictions of w phase stability beyond the hypothesis. The interaction between experimental work and theoretical modelling has allowed us to produce a master figure for the prediction of w stability in various TiAl-X systems. Excellent agreement exists between our prediction and experimental findings both by us and others.

TENSILE AND FATIGUE PROPERTIES OF HIPED GAMMA-TiAl PREALLOYED POWDERS AND EXTRUDED GAMMA-TiAl INGOTS. : *Hartmut Baur*[1]; Rainer Joos[1]; Nico Eberhardt[2]; Alexander Lorich[2]; Heinrich Kestler[2]; Helmut Clemens[3]; [1]Daimler-Benz AG, Research and Technology/Metals, Wilhelm-Runge Strasse 11, Ulm, Baden-Wuerttemberg 89013 Germany; [2]Plansee AG, Technology Center, Reutte, Tyrol A-6600 Austria; [3]Universitaet Stuttgart, Institut fuer Metallkunde, Seestrasse 71, Stuttgart, Baden-Wuerttemberg 70174 Germany

Abstract: Gamma-TiAl alloys are considered as potential materials for automotive components, e.g. valves. Two processing routes for valve production are under investigation, namely near-net shape processing of prealloyed powders via HIPing and single/multistep extrusion of cast ingots to rods which are subsequently hot-formed to final dimensions. In this paper the mechanical properties of rod materials are presented. The tensile properties of extruded material are superior to those of HIPed Material. The fatigue behavior was investigated at RT and 650ϒC, which corresponds to the brittle-to-ductile transition temperature. Due to their higher strength levels extruded material shows higher fatigue limits than the HIPed one. Also the scatter of the data is small in comparison to that of the HIPed material. This behavior is explained by the low portion of nonmetallic inclusions and microstructural inhomogeneities within the extruded material. Such imperfection are frequently observed in HIPed material, where they act as preferred sites for crack initiation.

MICROSTRUCTURE CONTROL AND LAMELLAR STABILITY IN A CAST TiAl AS A FUNCTION OF Mo AND C: *Ho-Nyun Lee*[1]; David Ray Johnson[1]; Haruyuki Inui[1]; Myung-Hoon Oh[2]; Dang-Moon Wee[3]; Masaharu Yamaguchi[1]; [1]Kyoto University, Dept. of Mat. Sci. & Eng., Yoshida Honmachi, Sakyo-ku, Kyoto 606-8501 Japan; [2]Kumoh National University of Technology, Dept. of Mat. Sci. & Eng., Shinpyung-Dong 188, Kumi, Kyungbuk 703-701 Korea; [3]KAIST, Dept. of Mat. Sci. & Eng., Gusong-Dong, Yusong-Ku, Taejon 305-701 Korea

The lamellar stability in a cast TiAl alloys containing small amounts (less than 1.5 at.%) of Mo and C were investigated in order to determine the processing window where the orientation of the lamellar microstructure could be controlled by directional solidification using a seeding technique. A partial liquidus surface near gamma TiAl was constructed for Ti-Al-Mo-C system. The lamellar stability was determined by quickly heating the material into the single phase alpha region, holding, and then cooling to room temperature. By maximizing the volume fraction of the alpha2 phase present at room temperature while ensuring that the alpha phase can form directly from the liquid, compositions for the seeding experiments were chosen such that original orientation of the lamellar microstructure was restored upon heating to and cooling from the melting temperature. Two prospective compositions were found in Ti-Al-Mo and Ti-Al-Mo-C systems and directional solidification of these alloys will be discussed.

PHASE STABILITY AND HIGH TEMPERATURE BEHAVIOR OF MOLYBDENUM AND BORON CONTAINING NEAR-GAMMA TITANIUM ALUMINIDES: *Julie Ann Christodoulou*[1]; Harvey M. Flower[1]; [1]Imperial College of Science Technology and Medicine, Dept. of Mats., Prince Consort Rd., London SW7 2BP UK

Both molybdenum and titanium diboride are of interest in the development of near-gamma titanium aluminide alloys. For example the diboride refines grain size while molybdenum introduces the ordered cubic B2 phase (Ti2AlMo) which may enhance ductility while providing high temperature capability. The effects are expected to be interactive as molybdenum can alter the boride chemistry and morphology and the overall phase equilibria. In the present work both these additions have been evaluated, principally in two multiphase alloys: Ti-50Al-5Mo+8vol%TiB2-particulates and Ti-44Al-8Mo+11(Ti,Mo)B whiskers. The combined influences of the phase stability, volume fraction and morphology on mechanical behavior at temperatures between 750ϒC and 900ϒC will be described.

DESIGNING CAST XD TiAl ALLOYS: PROS AND CONS: *Ji Zhang*[1]; [1]Central Iron and Steel Reserach Institute, Dept. of Superalloys, Beijing 100081 China

One of the present desires for cast TiAl alloys is now placed on producing refined cast lamellar microstructure, resulting in the development of the XD alloys containing certain amount of Boron. However, the positive and negative effects of the monolithic TiB2 particles in current XD alloys are rather difficult to be modified. In this paper, the compound additions of Boron and rare-earth element Nd are employed to generate hetergeneic refractory particles for grain refinement. The metallurgy and casting conditions will be taken into account as well. The prospect of designing the cast XD TiAl alloys to pursue the optimum grain refinement effectiveness without a negative effect on the ambient ductility will be discussed

ELECTROSLAG REMELTING OF GAMMA TiAl INGOTS: *Lev B. Medovar*[1]; Boris I. Medovar[1]; Boris B Fedorovskii[1]; Alexander V. Chernets[1]; [1]ELMET-ROLL, P.O. Box 259, Kyiv 252150 Ukraine

There ae several "ingot" technology for manufacturing of intermetallic compounds ingots: already tested and in use Vacuum Arc Remelting and Electron Beam Melting. ESR known as "ingot technology" with more flexibility than VAR or EBM and intendent for use like smelting method even before use like refining method. Were tested ESR smelting process with heat generation in slag pool by non-consumable electrode: so known current conductive mould. The results of process computer simulation and laboratory scale meltings of the TiAl (mainly 50%:50%) ingots will be discussed as well as some suggestion for the ESR using for industrial manufacturing of TiAl ingots.

A NOVEL PROCESS TO FABRICATE Ti/Ti ALUMINIDE LAMINATE COMPOSITE: *N. L. Richards*[2]; Mahesh C. Chaturvedi[1]; Weijie Wang[3]; Qiang Xu[1]; [1]University of Manitoba, Dept. of Mech. and Indust. Eng., 364 Eng. Bldg., Winnipeg, Manitoba R3T 2N2 Canada; [2]Bristol Aerospace Ltd., Materials/Processes, 660 Berry Street, Winnipeg, Manitoba R3C 2S4 Canada; [3]Lanzhou University, Department of Materials Science, Lanzhou, Gansu China

This paper will present our current research into fabrication technology of a Ti/Ti aluminide laminate composite using elemental Ti and Al foils. The fabrication process consisted of two steps: (1) a reaction sequence; (2) a post-reaction heating process. Influence of the first-step processing parameters including heating temperature, holding time, applied pressure and thickness of the starting Ti and Al foils on reaction between the Ti and Al foils was systematically investigated and thickness of the resultant Ti aluminide as a function of these parameters was established. The second-step process was also developed to remove residual porosity and close cracks that formed during the first step process. Post-processing heat treatment was employed to modify the microstructure in the Ti aluminide layer and the microstructural constituents in the Ti aluminide layer were characterised with TEM in detail. The results successfully demonstrated the potential of this technique for producing Ti/Ti aluminide composites.

EFFECT OF HOT-EXTRUSION ON MICROSTRUCTURE AND MECHANICAL PROPERTIES OF A TWO-PHASE TIAL ALLOY: *Michael Oehring*[1]; Uwe Lorenz[1]; Roland Niefanger[1]; Fritz Appel[1]; Richard Wagner[1]; Helmut Clemens[2]; Nico Eberhardt[3]; [1]GKSS Research

Center, Institut for Material Research, Max-Planck-Strasse, Geesthacht D-21502 Germany; [2]Universitaet Stuttgart, Institut fuer Metallkunde, Seestrasse 71, Stuttgart D-70174 Germany; [3]Plansee AG, Technology Center, Reutte A-6600 Austria

Cast ingots of a Ti-47at.% Al-(Nb, Cr, Mn, Si, B) alloy were hot-extruded in order to investigate the influence of processing conditions on microstructural development and the resulting mechanical properties. Hot-extrusion was performed over the temperature range 1250 - 1380ϒC on differently heat treated billets. Depending on extrusion temperature either fine equiaxed or refined lamellar microstructures were obtained. After hot-extrusion, compression and fracture mechanical tests were conducted with specimens parallel and perpendicular to the extrusion direction so that the effect of the texture as well as of an anisotropy in microstructure on the mechanical properties could be examined. It is found that the specimen orientation has no or only a relatively slight effect on the flow stress for alloys with equiaxed or refined lamellar microstructures, respectively. In contrast, the fracture toughness significantly depends on the specimen orientation for both types of microstructures.

PHASE EQUILIBRIA IN THE Al-RICH PART OF THE Al-Ti SYSTEM: *Martin Palm*[1]; Frank Stein[1]; [1]MPI fuer Eisenforschung GmbH, Phys. Metall., Max-Planck-Str. 1, Duesseldorf, NRW D-40237 Germany

According to the latest assessment of phase equilibria in the Al-Ti system, phase stability and phase equilibria at Al-contents above 55 at% Al are still not well established. This holds for the Al-rich phase boundary of g-TiAl as well as for the adjoining phases up to Al3Ti. It is known that between 65 at% and 75 at% Al a number of long-periodic superstructures exists. However, the exact number of compounds and their stability in dependence on composition and temperature has not been established. In order to clarify which phases do exist on the Al-rich side of the Al-Ti system and to establish the phase relations among these compounds, an experimental investigation was carried out. From diffusion couple experiments and investigation of equilibrated bulk alloys by metallography, X-ray diffraction, differential thermoanalysis and electron microprobe analysis the phase equilibria in the Al-rich part of the Al-Ti system were determined. The results are presented and discussed with respect to their significance for future alloy developments.

THE INFLUENCE OF NIOBIUM ON THE OXIDATION BEHAVIOUR OF TiAl-BASED INTERMETALLICS: *Marinus Frederik Stroosnijder*[1]; Jan Sunderkötter[1]; Vincent Haanappel[1]; [1]European Commission, Institute for Advanced Materials, Via Fermi 1, Ispra, VA 21020 Italy

The high temperature applications of gamma-TiAl based intermetallics are still limited by their corrosion resistance. Improvement of the corrosion resistance can be obtained by alloying. Particularly, small additions of niobium may exhibit beneficial effects on the oxidation resistance. A general overview of the effects of niobium additions on the oxidation behaviour of TiAl-based alloys will be given in the presentation. Experimental results using alloying and ion implantation in combination with advanced techniques, such as isotope tracer techniques will be presented. The mechanisms proposed in the literature to explain the niobium effects are critically discussed in view of the presented experimental results. Suggestions for clarification of the underlying mechanisms are given.

VARIATIONS IN THE MECHANICAL BEHAVIOR OF SINGLE CRYSTALLINE GAMMA-TiAl AS A FUNCTION OF ALUMINUM CONTENT: *Marc Zupan*[1]; K. J. Hemker[1]; [1]The Johns Hopkins University, Mech. Eng., 122 Latrobe Hall, 3400 North Charles St., Baltimore, MD 21218 USA

Dislocation activity in two-phase commercial TiAl alloys occurs most readily in the γ-TiAl phase, and measurements of the CRSS of γ-TiAl are needed to provide a solid foundation for modeling the mechanical performance of these alloys. Single crystal studies of γ-TiAl with greater than 55%Al have been forth coming, but differences between the results of these works and studies involving polycrystalline and two-phase alloys suggest that the underlying deformation mechanisms vary with Al content. Single crystals of γ-TiAl cannot be grown near the stoichiometric composition, but microsample tensile specimens have been machined from within very large single grains of overaged polycrystalline Ti-52%Al. The dependence of the CRSS on crystallographic orientation, temperature and Al content, as measured with single crystalline microsamples, will be discussed. TEM observations are being used to identify the controlling deformation mechanisms for both alloys, and comparisons will be made with current dislocation theories for γ-TiAl.

STUDY OF FRACTURE ORIGINS IN GAMMA-TiAl ALLOYS USING DISPLACEMENT MAPPING AND MICROSTRUCTURAL CHARACTERIZATION: *Nicholas E. Biery*[1]; Rafael Raban[1]; Tresa M. Pollock[1]; Marc De Graef[1]; [1]Carnegie Mellon, Dept. of Mats. Sci. and Eng., 5000 Forbes Ave., Pittsburgh, PA 15213-3890 USA

Gamma-TiAl alloys are potential replacements for nickel-based alloys in engine applications. However, the modest ductility of these alloys is of concern, particularly in the vicinity of stress concentrators. An understanding of the events leading to fracture may help address these concerns by identifying desirable and undesirable features, which can be taken into account during alloy and component design. The strain mapping technique measures the surface components of the displacement of arrays of markers deposited on notched samples (250 micron notch radius). The markers are deposited by evaporation of gold or platinum through a commercially available 1500 mesh Ni grid. A pattern recognition algorithm is then used to locate the individual markers with sub-pixel resolution. Strain components are computed from the displacement components. Superposition of strain contours on scanning electron micrographs and maps obtained by orientation imaging microscopy then facilitates the correlation of microstructural features with strain localization and fracture. Strain mapping experiments reveal highly localized strains in large, favorably oriented gamma grains near the notch root. Subsequent transgranular fracture was commonly observed to initiate in these grains. This research was funded by AFOSR grant # F49620-95-1-0359.

HOT DEFORMATION OF GAMMA TiAl ALLOYS: FUNDAMENTALS AND PRACTICE.: *Renat Imayev*[1]; Gennady Salishchev[1]; Marat Shagiev[1]; Andrey Kuznetsov[1]; Fritz Appel[2]; Fritz Appel[2]; Fritz Appel[2]; Michael Oehring[2]; Valery Imayev[2]; [1]Institute for Metals Superplasticity Problems, Russian Academy of Sciences, Khalturina Str., 39, Ufa, Bashkortostan 450001 Russia; [2]Institute for Materials Research, GKSS Research Centre, Max-Planck-Str., Geesthacht, D-21502 Germany; [2]Institute for Materials Research, GKSS Research Centre, Max-Planck-Str., Geesthacht, Germany D-21502 Germany; [2]Institute for Materials Research, GKSS Research Centre, Max-Planck-Str., Geesthacht, Germany D-21502 Germany

Microstructural and chemical homogeneities are determinant for obtaining the high-quality parts of gamma TiAl alloys. One of the effective ways of homogeneity improvement is hot deformation including the grain refinement due to the dynamic recrystallization occurrence and the considerable improvement of microstructural and chemical homogeneities due to superplastic processing. In this talk, the following questions will be discussed: Effects of the material preparing techniques (cast, powder metallurgy) and the preliminary heat treatment on the dynamic recrystallization kinetics and chemical (phase distribution)homogeneity; Effects of Al content, alloying, grain size and lamellae orientation on the deformation mechanism and kinetics of dynamic recrystallization; The reasons leading to the striped microstructure formation and the possible ways of its avoidance; Formation of submicro- and microcristalline (d~0.1 and 1 mkm, respectively) structure in largescaled billets by means of multiple isothermal forging and isothermal equal channel angular extrusion under superplastic conditions.

TITANIUM ALUMINIDE POWDER PRODUCTION VIA REACTION BETWEEN TiCl4 AND Al: *Stephen J. Gerdemann*[1]; David E. Alman[1]; [1]Albany Research Center, Dept. of Energy, 1450 Queen Ave. SW, Albany, OR 97321 USA

TiAl is emerging as a candidate material for applications at elevated temperatures and in aggressive environment. This is being driven by the low specific properties and superior oxidation resistance of the compound compared to titanium alloys. For utilization of this material beyond a few highly specialized applications (e.g., aerospace/defense), new cost effective methods for producing TiAl components are re-

quired. This includes powder metallurgical and powder production unit operations. The present paper discusses the feasibility of producing TiAl by reacting TiCl4 and Al. This is similar to the well known Kroll process to produce Ti sponge from TiCl4 and Mg. Thermodynamic calculations show that above 600ϒC it is possible to produce TiAl from TiCl4 and aluminum. At lower temperatures AlTi3 is favored and TiCl4 is only reduced to TiCl2. Above 650ϒC TiCl4 utilization is improved but aluminum melts at 660ϒC. The results of the thermodynamic analysis were used to design experiments and the results of the experiments are compared with the thermodynamic analysis. Some ideas on the possibility of making inexpensive (i.e., <$3.00/lb) TiAl powder by this route are evaluated.

HIGH TEMPERATURE OXIDATION OF GAMMA TiAl ALLOYS: INFLUENCE OF REFRACTORY AND RARE EARTHS ELEMENT ADDITIONS: Stefano Gialanella[1]; Mohamed Nazmy[2]; Marc Staubli[2]; *Andrea Tomasi*[3]; [1]Università di Trento, Dipartimento di Ingegneria dei Materiali, Mesiano, Trento 38100 Italy; [2]ABB Power Generation, Gas Turbine Development, Baden 5401 Switzerland; [3]Istituto di Ricerca Scientifica e Tecnologica, Via Sommarive, Povo, Trento 38050 Italy

A number of alloy compositions and tempers have been considered in the research efforts carried out to get better gamma TiAl base alloys. Mechanical properties have been considered so far as main guidelines for alloy development. However, the increasing temperature capabilities achieved with the latest formulations of TiAl alloys have made of surface durability and, particularly, oxidation resistance a main issue for a valuable and reliable application of these materials. In the present study several alloys have been considered with respect to the isothermal oxidation behaviour in air over the 600-800°C temperature range. The effect of such alloying elements as W, Ta and Zr has been considered when added to base compositions containing Cr, Si and Y. The study, carried out using conventional thermoanalytical and microscopic investigation techniques, provides preliminary indications about the role the different elements play in improving the oxidation resistance of these promising alloys.

ROLE OF TITANIUM SILICIDES ON CREEP STRENGTH OF Si BEARING TiAl ALLOYS: Seung Eon Kim[1]; [1]Korea Institute of Machiney and Materials, Mats. Eng., 66 Sangnam, Changwon, Kyungnam 641-010 Korea

Prominent creep strength of Si bearing TiAl base alloys has been well known. Si addition to TiAl alloys inevitably yields Ti5Si3 type silicides. Precipitation hardening effect by the titanium silicides has been generally recognized in improving creep resistance. Unlike this, recently, solid solution hardening effect by Si itself has been also asserted to be dominant rather than precipitation strengthening. Another interesting report showed that strain assisted silicides are produced during creep test and enhance creep strength. So far, the creep strengthening mechanism by Si addition seems controversial. In this study, a systematic data for the effect of Si content on creep properties of Ti52Al48 base alloys will be depicted. From the results, role of titanium silicides on creep properties will be discussed and strengthening mechanism will be clarified.

INFLUENCE OF GASEOUS SPECIES ON THE OXIDATION BEHAVIOUR OF TiAl AT HIGH TEMPERATURES: *S. Taniguchi*[1]; [1]Osaka University, Dept. of Mats. Sci. and Proc., Graduate School of Engineering, 2-1 Yumadaoka, Suita, Osaka 565 Japan

TiAl coupon specimens were oxidized in various gas mixtures, O2-H2O, O2-CO2 and O2-N2, and in the constituent single gases under atmospheric pressure at 1100 and 200 K for up to 100 ks. Conventional metallographic examinations were performed for characterizing the oxidation products, using X-ray diffractometry, scanning electron microscopy combined with energy dispersive X-ray spectroscopy and so on. All the gases added to oxygen significantly enhance the oxidation, with the influence decreasing in the following order, water vapour, carbon dioxide and nitrogen. The addition of water vapor and carbon dioxide disturbs the sintering of oxide grains resulting in a fine porous structure in the inner scale layer. When carbon dioxide was added, TiC was found near the scale/substrate interface in the scale and rutile crystals in the outer scale layer show characteristically stepped structure implying the directional mass transport through them.

EFFECT OF LONG TERM STATIC AND CYCLIC THERMAL EXPOSURE ON THE MICROSTRUCTURAL STABILITY OF Ti-44Al-11Nb ALLOY: Carlos Hernandez[1]; Erica Corral[1]; Alvaro Chan[1]; Rabindra Mahapatra[2]; *Shailendra K. Varma*[1]; [1]The University of Texas at El Paso, ept. of Metall. and Mats. Eng., El Paso, TX 79968-0520 USA; [2]Naval Air Warfare Center, Aircraft Division, Patuxent River, MD 20670 USA

Polycrystalline and aligned crystals of Ti-44Al-11Nb alloy have been subjected to oxidation environment in air at 900, 950 and 1000oC for a period of about one week. One cycle is defined as 55 minutes of heating and then 5 minutes cooling in air and has been continued for up to seven days or longer. Static mode consists of continuous heating of the sample in the furnace without interruption for similar periods of time. Cyclic mode appears to indicate lower rate of oxidation due to the necessity of recreating the diffusive paths after every cycle. Oxidation penetration in to the alloy follows a crystallographic direction parallel to the alternate lamellar directions of a2 and g phases in the microstructure. Large number of dislocations have been found to be generated during cyclic heating and semicoherent O-phase has been observed at 1000oC.

FRACTOMETRY OF TWO DIFFERENT TiAl-MICROSTRUCTURES: *Thomas Hebesberger*[1]; Christopher Semprimoschnig[1]; Reinhard Pippan[1]; Otmar Kolednik[1]; Helmut Clemens[2]; [1]Austrian Academy of Sciences, Erich-Schmid-Institut for Material Science, Jahnstr. 12, Leoben, Styria 8700 Austria; [2]Univ. of Stuttgart, Inst. f. Metallkunde, Seestrasse 71, Stuttgart 70174 Germany

In this study the fracture behaviour of a Ti - 46.5Al - 4(Cr,Nb,Ta,B) alloy is investigated in the temperature range between -196ϒC and 700ϒC. Two different microstructures are tested: a coarse-grained fully lamellar $\gamma + \alpha_2$ microstructure (FL) and a fine-grained near γ microstructure (NG). For both microstructures impact bending tests are performed, as well as conventional fracture mechanics tests. Conventional fractographic studies revealed that specimens with the NG microstructure change their fracture mode with increasing temperature from transcrystalline to intercrystalline fracture. Specimens with the FL microstructure, however, fail predominantly in a translamellar mode. For a more thorough inspection of the fracture surfaces the crystallographic fractometry is applied. This is a new tool for the analyses of cleavage fracture surfaces, which is based on the combination of crystal orientation measurements with electron backscatter diffraction (EBSD) and the automatic reconstruction of fracture surfaces from stereo-image pairs [1]. The technique allows the measurement of the spatial orientation of cleavage facets and their crystallographic indication. It is found that for the FL microstructure different cleavage planes are activated in the two different fracture tests: In the broken fracture mechanics specimens the predominant cleavage facets lie in the α_2 phase having a {0001} orientation. Contrarily, in the impact bending specimens cleavage planes with {111} orientation inside the γ-phase are activated. For the NG microstructure no such difference was observed in the fracture behaviour between the impact bending and the fracture mechanics tests. The material was kindly provided by the PLANSEE AG, Austria. Semprimoschnig C.O.A. et. al: "A new powerful tool for surveying cleavage fracture surfaces", Fatigue & Fracture of Engineering Materials & Structures, Vol. 20 No. 11, 1997, pp. 1541-1550.

CHEMICAL COMPOSITION EFFECTS UPON CREEP STRENGTH OF GAMMA-BASE TITANIUM ALUMINIDES ALLOYED WITH VANADIUM: *Tohru Takahashi*[1]; Toshiaki Sujino[2]; Yoshihiro Abe[2]; Tadashi Hasegawa[1]; [1]Tokyo University of Agriculture and Technology, Dept. of Mech. Syst. Eng., Naka-cho 2-24-16, Koganei, Tokyo 184-8588 Japan; [2]Tokyo University of Agriculture and Technology, Graduate School, Naka-cho 2-24-16, Koganei, Tokyo 184-8588 Japan

Creep strength is one of critical parameters for materials applied in heat resisting structures. In the present study, creep characteristics have been investigated in gamma-base titanium aluminides of aluminum-titanium-vanadium ternary compositions. Aluminum content varied from 50 to 60 at.%, and vanadium was added up to 25 at.%, and the remainder was titanium. A small amount of beta phase was present in materials with higher vanadium content. In order to characterize the effect of vanadium content upon creep strength, compressive creep tests were carried out in recrystallized polycrystals with various compositions.

Minimal value in minimum creep rates was found at 5 at.% V and 10 at.% V in 50 at.% Al and 55 at.% Al materials, respectively. Creep strength decreased in the materials containing higher vanadium, probably due to the presence of beta phase which seemed to be weaker than the gamma phase at high temperatures.

GAMMA TITANIUM ALUMINIDE DEVELOPED BY INTERDIFFUSION OF MULTI-LAMINATED COMPOSITES OF TITANIUM AND ALUMINUM: *Jian-Guo Luo*[1]; Viola L. Acoff[1]; [1]The University of Alabama, Metall. & Mats., P.O. Box 870202, Tuscaloosa, AL 35487-0202 USA

Multi-laminated sheets of pure titanium and aluminum were prepared by cold-bonding and annealing at various temperatures and times. The technique of developing gamma titanium aluminide from the interdiffusion process between titanium and aluminum were examined by scanning electron microscopy (SEM) equipped with energy dispersive spectroscopy, x-ray diffraction and light microscopy. Based upon these examinations, the active energy and mechanism of interdiffusion between titanium and aluminum, the interdiffusion coefficients and the reaction kinetics were determined for different annealing temperatures and imes were determinated. The mechanical properties of the resulting gamma titanium aluminide layers were determined using microhardness and nanoindentation testing. Results of this study show that TiAl3 forms during the developing process for gamma titaniu aluminides. A two-stage annealing process, in which one is at higher temperature and longer time, is needed in order to develop higher level gamma titanium aluminides. The research also confirmed the interdiffusion of titanium and aluminum is a parabolic growth process controlled by volume diffusion.

CREEP BEHAVIOR OF A CAST TiAL-BASE ALLOY FOR GAS TURBINE BLADE APPLICATION: *Valentino Lupinc*[1]; Wei-Min Yin[2]; Maurizio Maldini[1]; [1]CNR-TEMPE, Via Cozzi 53, Milan 20125 Italy; [2]Institute of Metal Reserach, 72 Wenhua Road, Shenyang 110015 PR China

Creep behavior of various batches of the Ti-47Al-2W-0.5Si cast alloy having small composition variations has been examined. The microstructure, that strongly influences the creep resistance, was found to vary with composition, solidification path and heat treatment region in the phase diagram. In particular the creep behavior of the most creep resistant duplex microstructure material is described in detail, trying to define some physical parameters controlling the minimum creep rate, and interpolated within the experimentally explored range. The duplex microstructure consists mainly of lamellar gamma/alpha2 colonies, a smaller amount of globular gamma grains, and also some secondary beta and silicide phases, and provides a good compromise of mechanical properties when solidification occurs through the b phase. Stress-rupture and creep resistances of this cast alloy are compared to the properties of some other TiAl base alloys and to the density corrected IN738LC stress-rupture behavior.

HIGH TEMPERATURE LOW CYCLE FATIGUE PROPERTIES OF Ti-45Al-2Nb-2Mn+0.8vol.% TiB2 AND Ti-47Al-2Nb-2Mn+0.8vol.% TiB2 IN SITU GAMMA TITANIUM ALUMINIDE COMPOSITES: *Viktor Recina*[1]; [1]Volvo Aero Corporation, Mats. R&D, Maloga, Trollhattan, Vastergotland 461 81 Sweden

Low cycle fatigue testing of Ti-45Al-2Nb-2Mn+0.8vol.% TiB2 and Ti-47Al-2Nb-2Mn+0.8vol.% TiB2 in situ gamma titanium aluminide composites is going to be performed at 600ϒC in fully reversed push-pull mode (R=-1) with a triangular wave form. The microstructures of the two alloys are going to be characterized through optical and scanning electron microscopy. The fracture surfaces will be investigated to elucidate the fracture initiation and growth behavior. Both the fracture behavior and the fatigue performance will be correlated to the microstructure. The fatigue properties and behavior will be compared to previous low cycle fatigue testing of monolithic gamma titanium aluminide alloys tested at similar conditions. The low cycle fatigue testing is planned to be finished in the end of May, 1998, the evaluation will be finished not later than August, 1998.

THE INFLUENCE OF VARIOUS ALLOYING ADDITIONS ON Z-PHASE STABILISATION AND THEIR ROLE IN THE OXIDATION BEHAVIOUR OF GAMMA-TiAl BASED ALLOYS.: *Vladimir Shemet*[1]; Lorenzo Singheiser[1]; *Willem Joe Quadakkers*[1]; *Willem Joe Quadakkers*[1]; [1]Forschungszentrum Juelich, Institute for Materials in Energy Systems, Juelich D-52425 Germany

The high temperature oxidation behaviour of gamma-TiAl intermetallics containing various alloying additions has been studied in air and oxygen at 800-900ϒC. It was found that alloying elements can have a beneficial effect on the oxidation resistance of gamma-TiAl intermetallics in two ways: I) reducing the growth rate of the mixed TiO2/ Al2O3 scale; II) promoting protective Al2O3 formation. The beneficial effect of Nb, Mo, W, Sc and La additions are related to modification of the properties of the mixed scale (mechanism I). The alloying elements (Ag, Cr, Zr and Hf) promote formation of a protective alumina based scale. This is due to stabilisation of the ternary Z-phase (Ti5Al3O2) beneath the scale. The best long term oxidation resistance for temperature up to 900ϒC in Ar/O2 was obtained for gamma-TiAl alloys containing small additions of both Zr and Nb. For interpreting the beneficial or detrimental effect of alloying addition on gamma-TiAl alloys oxidation, the significant of the composition of the test atmosphere (oxygen or air) has to be considered. It was found that presence of nitrogen in the oxidation atmosphere is in some cases detrimental, in others beneficial. For gamma-TiAl based alloys, which tend to form alumina based scale, nitrogen always seems to be detrimental because it retards the Z-phase formation in the Al-depletion layer. As a result it promotes the formation of more rapidly growing, mixed Al2O3/TiO2 scales. A beneficial effect of nitrogen was found for gamma-TiAl based alloys which tend to show internal oxidation of aluminium. The nitride layer which is forming at the scale/alloy interface prevents this process. The presents results indicate, that long term protective alumina formation can be obtained by alloying elements which stabilize the Z-phase as well as prevent the formation of Ti-rich nitrides beneath the alumina scale.

MICROSTRUCTURAL MODIFICATION OF INVESTMENT CAST Ti-47Al-2Nb-1Mn-0.5Mo-0.5W-0.2Si ALLOY BY HEAT TREATMENT: *Weijie R. Chen*[1]; Jonathan Beddoes[1]; Linruo Zhao[2]; [1]Carleton University, Dept. of Mech. & Aero. Eng., 1125 Colonel By Dr., Ottawa, Ontario K1S 5B6 Canada; [2]National Research Council of Canada, Structures, Materials & Propulsion Lab., Institute For Aerospace Research, Montreal Road, M-13, Ottawa, Ontario K1A 0R6 Canada

The modification of the columnar cast duplex structure of a complex investment cast gamma alloy via heat treatment is presented. An innovative primary heat treatment process is applied to cast bars to develop an equiaxed fully lamellar structure while preventing minor phase precipitation and the formation of massively transformed g. The resulting fully lamellar structure has relatively fine lamellar interface spacing that is dependent on the homogeneity of the cast structure, and well interlocked lamellae along lamellar grain boundaries. It is believed that these features will enhance elevated temper-ature properties. An advantage of the primary heat treatment profile utilized is the ability to control the formation of minor phases precipitated during a secondary heat treatment process. Minor phase precipitates are enriched in Nb and Si, and precipitate primarily along lamellar interfaces. The formation of the precipitates is also strongly dependent on the compositional segregation of the cast material.

DEFORMATION BEHAVIOUR OF GAMMA TITANIUM ALUMINIDES - MICROMECHANICAL MODELLING OF SINGLE PST CRYSTALS AND POLYCRYSTALLINE MATERIALS: *Wilfried Thomas Marketz*[1]; Franz Dieter Fischer[1]; *Helmut Clemens*[2]; [1]Montanuniversitaet Leoben, Institut fuer Mechanik, Franz-Josef-Strasse 18, Leoben A-8700 Austria; [2]Universitaet Stuttgart, Institut fuer Metallkunde, Seestrasse 71, Stuttgart D-70174 Germany

The mechanical properties of γ-TiAl based two phase alloys consisting of the γ-TiAl phase and a small volume fraction of the α2-Ti3Al phase are determined by the microstructure. The deformation characteristics are simulated by a three dimensional model based on the unit cell technique using the finite element method [1]. This model considers crystallographic slip and deformation twinning as the deformation mechanisms in addition to the elastic behaviour. The microstructure and the crystallography are incorporated by the framework of crystal plasticity. Initially, this micromechanical concept was applied to single polysynthetically twinned (PST) crystals of TiAl. The results of the

simulation reflect the anisotropic plastic behaviour of the lamellar microstructure which was experimentally observed, too. Since it has been shown that the chosen micromechanical model reproduces the deformation mechanisms in a proper way, the concept was now extended to polycrystalline material. In order to start with a rather simple case, a so called near gamma microstructure was chosen. Furthermore it was demonstrated that only a fully three-dimensional modelling delivers reasonable predictions.[1] S.M. Schloegl: Micromechanical modelling of the deformation behaviour of gamma titanium aluminides, Fortschritts-Berichte VDI, Reihe 18: Nr. 220,1997.

FATIGUE INITIATION IN NEAR-LAMELLAR 3-95 (Ti-46Al-2Nb-2Cr-1Mo-0.2B): *W. John Porter*[1]; Kezhong Li[1]; David C. Maxwell[1]; Andrew Rosenberger[2]; James M. Larsen[2]; [1]University of Dayton Research Institute, Structural Integrity, 300 College Park, Dayton, OH 45469-0128 USA; [2]United States Air Force, Air Force Research Labs, 2230 Tenth Street, Ste. 1, WPAFB, OH 45433-7817 USA

Gamma titanium aluminides are being considered for application as rotating components in aerospace turbine engines. To increase the likelihood of gamma application, a thorough understanding of the relationship between microstructure and fatigue initiation is required. This study investigated the fatigue performace of a wrought, near-lamellar gamma alloy, 3-95 (Ti-46Al-2Nb-2Cr-1Mo-0.2B), at RT, 540 and 700ºC tested at stress ratios of 0.1 and 0.6. Up to five samples per stress level were tested in order to determine the causes for data scatter. Detailed fractography was perfomed to determine the mechanisms leading to initiation. A comparison of the results from this alloy are made to other current gamma alloys tested under similar conditions.

THE FUTURE USE OF GAMMA TITANIUM ALUMINIDES BY ROLLS-ROYCE: *Wayne E. Voice*[1]; [1]Rolls-Royce Plc, Aero-Engine/ Materials, Elton Rd., (ELT-38), P.O. Box 31, Derby, Derbyshire DE24 8BJ UK

Gamma TiAl is essential for meeting military and civil engine performance targets in the future and potentially it could be used throughout the engine from the compressor to turbine. The current Rolls-Royce alloy is the established Ti-45-2-2-XD and this is competing for lower temperature applications such as stators and structural components which take advantage of the lower costs arising from the casting route. Rigorous design criteria are required to compensate for the risks in using these relatively new materials in components and this requires investigation into the effects of manufactured surface conditions, of microstructures local to load bearing regions and of compositional variations. For the future, Rolls-Royce has patented a number of next generation cast titanium aluminides resulting from alloy development programmes undertaken by Birmingham University. These aim to optimise castability with strength and creep resistance and their potential for commercial use within the aero-engine will be discussed.

MICROSTRUCTURAL CHARACTERIZATION OF LASER-DEPOSITED TiAl ALLOYS: *Xiao-Dong Zhang*[1]; Richard Grylls[1]; Dan Evans[2]; Hamish Fraser[1]; [1]The Ohio State University, Dept. of Mats. Sci. and Eng., 2041 College Rd., Columbus, OH 43210 USA; [2]Wright Patterson AFB, Wright Laboratory, WL/MLLM, Dayton, OH 45433 USA

Several TiAl alloys have been laser deposited using Laser Engineered Net Shaping (LENS) technology. LENS is a laser direct metal deposition process that combines laser cladding technologies with advanced rapid prototyping methods with capability to directly manufacture complex three-dimensional components. Different microstructure can be obtained depended on the processing parameters (laser scan speed, powder feed rate and pressure, subtract materials and post heat treatment). A number of high temperature metastable phases, such as a and b phases, have been retained at room temperature. By careful control of post heat treatment, we can optimize the microstructure and mechanical properties. Significance of the LENS technique will be discussed in terms of near net-shape manufacture, microstructural control and potential applications.

THE FRACTURE MECHANISM STUDY OF PST CRYSTAL THROUGH IN-SITU OBSERVATION: Yonggang Zhang[1]; [1]Beijing University of Aeronautics and Astronautics, Dept. of Mats. Sci. and Eng., 37 Xueyuan Rd., Haidian, Beijing 100083 China

The fracture mechanisms of PST crystals of Ti-49at.%Al in different orientations have been investigated through in-situ observations by both SEM and TEM. The results showed that the fracture behavior and mechanisms are strongly dependent on the angle of loading axis to the lamellae and controlled by ability of dislocation emission ahead of crack tip. When the loading axis is parallel to the lamellae, the crack propagated transversally by nucleation, growth and linkage of microcracks, and the main crack could be blunted by interface sliding and emission of ordinary dislocations and twinning. When the loading axis is perpendicular to the lamellae, the crack propagated along the interfaces and the tip kept sharpness, and no dislocations were emitted ahead of the crack tip. The results were analyzed micromechanically with the particular attention on stress distributions and toughness mechanism.

MICROCRACKING IN POLYSYNTHETICALLY TWINNED (PST) TiAl CRYSTALS UNDER COMPRESSION:: *Zhe Jin*[1]; Carl M. Cady[1]; George T. Gray[1]; Masaharu Yamaguchi[2]; Masaharu Yamaguchi[2]; [1]Los Alamos National Laboratory, Mats. Sci. and Tech., MST-8, MS G755, Los Alamos, NM 87545 USA

Microcracking behavior of polysynthetically twinned (PST) TiAl crystals under a compressive loading condition was studied at different strain rates and temperatures. The microcracking was observed to start at very small strains at room temperature for all strain rates studied, ranging from 0.001/s to 3000/s. The interlamellar microcracks were formed primarily due to a mismatch shear stress across lamellar interfaces, which depended on the deformation of individual domains on these interfaces. The translamellar microcracks were observed to be a mode-I type crack. As the testing temperature increases, the formation of microcracks was observed to be delayed in terms of strain.

LEACHING THEORY PROCESS DEVELOPMENT & INDUSTRIAL PRACTICE: Pressure Leaching

Sponsored by: Extraction & Processing Division, Aqueous Processing Committee, Copper, Nickel, Cobalt Committee
Program Organizers: Akram Alfantazi, Falconbridge, Ltd., Falconbridge Technology Centre, Falconbridge, Ontario P0M 1S0 Canada; Arash Kasaaian, Elkem Metals Company, Marietta, OH 45750 USA; Alexandre J. Monteiro, Indosuez Capital Emerging Markets, Sao Paulo, SP 01311-902 Brazil

Tuesday PM — Room: 1B
March 2, 1999 — Location: Convention Center

Session Chairs: Dr. D. Dreisinger, UBC; C. Fleming, Lakefield Research

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THE BEHAVIOR OF ORPIMENT DURING PRESSURE OXIDATION: PART 1, CHEMISTRY: *Hu Long*[1]; David G. Dixon[1]; [1]University of British Columbia, Dept. of Metals and Mats. Eng., 309-6350 Stores Rd., Vancouver B.C. V6T 1Z4 Canada

In this, the first systematic study of the oxidation of orpiment (As_2S_3) in sulfuric acid solution under oxygen pressure at temperatures above 170ºC, the efforts of temperature, particle size oxygen parietal pressure, the concentration of sulfuric acid and pulp density were evaluated The effect of ferric ion addition was also examined. The products of oxidation are As (III), As (V), SO_4^{2-} and elemental sulfur. At temperatures ranging from 170 to 230ºC, most of the arsenic was found to in the trivalent state, and oxidation to As (V) with oxygen was very slow. This was confirmed by attempting to oxidize a synthetic arsenious solution. However, the rate of oxidation of As (III) to As (V) is rapid in the

presence of ferric ion. Elemental sulfur was found at all temperature investigated except at 230ϒC.

2:50 PM

PRESSURE LEACHING OF NIOBIUM AND TANTALUM FROM COLUMBO-TANTALITES: *M. Ruiz*[1]; C. Rodriquez[1]; M. Gonzalez[1]; J. Rivarola[1]; [1]Universidad Nacional de San Luis-CONICET, Instituto de Investigaciones en Tecnologia Quimica (INTEQUI), Casilla De Correo 290, San Luis Argentina

The extraction of niobium and tantalum with hydrofluoric acid from a columbo-tantalite of San Luis (Argentina) using a pressure Parr reactor of 450 ml, made of monel, is being studied. The reagents, products and residues have been characterized by techniques such as SEM, FRX, ICP-AES, BET and particle size analysis. The effect of the following variables on recovery has been studied: temperature, reaction time, acid concentration, pulp stirring rate, particle size and solid-liquid ratio. Results indicate that Nb and Ta extractions increase with increasing reaction time at 75ϒC. For higher temperatures the extraction grows until 90 minutes and for longer times the extraction values decreases They are not markedly affected by the stirring rate in the interval studied. Decreasing particle size, from +80 to -325 mesh, does not considerably improve extraction levels. Increasing solid concentration causes a decrease of the amounts of metals recovery. The ICP-AES analysis of the reaction products show that there is strong dissolution of niobium, tantalum, iron and manganese contained in the mineral. These results might indicate that Nb and Ta extraction is a consequence of a dissolution process of all the particles in the mineral. The XRD diagrams of the residues did not show formation of new crystalline structures but the minerals accompanying de columbo-tantalite (quarz, muscovite and feldspar) almost totally disappeared. FRX analysis of the residues showed that 1) for the least energetic working conditions, the amounts of Nb, Ta, Fe and Mn remaining in the residues correspond to the mineral stoichiometry, which would indicate a uniform attack on all the particle; 2) the residues treated at higher temperatures and longer reaction times show a slight enrichment in Ta.

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DESIGN OF PRESSURE HYDROMETALLURGICAL PROCESS PLANTS: *F. Campbell*[1]; L. Trytten[1]; W. D. Vardill[1]; [1]Dynatec Corporation, Metall. Tech. Div., P.O. Box 17, 10103-114 St., Fort Saskatchewan, Alberta T8L 2WI Canada

More than 45 years of experience in the scale up of pressure hydrometallurgical processes are reviewed from pioneering collaboration between Sherrit and Chemical Construction Company to process development in the present by their successor Dymatec Corporation. The evolution of testwork is discussed, from traditional pilot plant operations using semi-commercial equipment to small scale or minipiloting with equipment several thousand times smaller than commercial units. Nickel, uranium, zinc acid gold processes have been developed and successfully implemented in world scale operations, treating a variety offered materials including concentrates, ores and mattes. Historical data on testwork duration and ramp up of several commercial plants are presented.

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SULPHURIC ACID PRESSURE LEACHING OF LATERITES - METAL SOLUBILITIES AND SPECIATION ANALYSIS: *D. H. Rubisov*[1]; V. G. Papangelakis[1]; [1]University of Toronto, Dept. of Chem. Eng. and Applied Chem. 200 College St., Toronto, Ontario M5S 3E5 Canada

Sulphuric acid pressure leaching of nickeliferous laterites has attracted an attention from the nickel industry. This process allows for recovering nickel and cobalt by rejecting iron and aluminum in the same time. The process is especially advantageous for linmonitic laterites that mostly contain ferric oxo-hydroxide because iron precipitates releasing acid and thus rendering low acid consumption. It is also applicable to mixtures of linmonites and saprolites. Effective process design requires the solubility of metals that may precipitate during the process to be known. In the present work, determination of metal solubilities is based oil a simple specification program that assumes the presence of only a dominant complex for each metal. The thermodynamic data for the precipitation reactions are extracted from high-temperature experiments with monometallic systems published previously. The validity of the approach is then tested against mixed bimetallic systems, and finally applied to calculate the solubility of aluminium, iron and magnesium is laterite leaching effluents at temperature. In both cases of limonitic feed and lirnonitic/saprolitic blends, the prediction closely follows metal solubilities measured experimentally at temperatures from 230 to 270ϒC and at terminal free acidities ranging from 0.1 to 0.7 mol/1.

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PRESSURE LEACHING OF LAS CRUCES COPPER ORE IN THE DYNATEC MINIPLANT: *T. Xue*[1]; M. Collins[1]; M. Makwana[1]; J. MacLean[2]; I. Barton-Jones[2]; M. Southgate[2]; [1]Dynatec Corporation, Metall. Tech. Div., P.O. Box 17, 10103-114 St., Fort Saskatchewan, Alberta T8L 2W1 Canada; [2]Rio Tinto Technical Services, Castlemead, Lower Castle St., Bristol BS99 7YR UK

A hydrometalluical process has been developed for treating ore of the Las Cruces massive sulphide deposit located near Seville, Spain. A two-stage countercurrent leach process, consisting of an atmospheric leach and a pressure leach, has been developed to effectively leach copper from the copper-bearing minerals and to generate a solution suitable for the subsequent solvent extraction and copper electrowinning operation. The results of batch and continuous miniplant tests are presented.

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PRESSURE HYDROMETALLURGY, NO LONGER REGARDED WITH TREPIDATION FOR THE TREATMENT OF GOLD AND BASE METAL ORES AND CONCENTRATES: *Peter G. Mason*[1]; Jim W. Gulyas[2]; [1]Highlands Pacific, Ltd., Brisbane Queensland; [2]H. A. Simons, Ltd., Suite #400, 111 Durnsmuir St., Vancouver, British Columbia Canada

Over the last 15 years numerous Pressure Oxidation and Pressure Leach plants have been installed throughout the world. The technology is no longer regarded with awe and trepidation as plants designed to treat a wide range of feedstocks continue to be successfully brought on line. Important aspects of the design of such plants include feed preparation, slurry pumping, heating and heat recovery, pressure control and let-down, vessel design and provision of associated services.

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STOICHIOMETRIC AND KINETICS EFFECTS ON THE PRESSURE LEACHING OF ZINC CONCENTRATES: G. P. Demopoulos[1]; S. A. Baldwin[2]; [1]McGill University, Department of Mining and Metallurgical Engineering, 3610 University Street, Montreal, QC H3A 2B2, Canada; [2]University of British Columbia, Department of Chemical & Bioresource Engineering, Vancouver, B.C., Canada

Zinc pressure leaching is a very complex reaction system with the main reactions being oxygen mass transfer, oxidation of ferrous to ferric iron, ferric ion leaching of marmatite, and iron precipitation; the oxidation of other sulphide minerals present in the concentrate is a further complicating factor as is the small (but critical) conversion-oxidation of sulphur to sulphate. In literature the individual kinetics of all main reactions of this system have been published following investigations involving in general dilute mineral slurries in small bench scale batch reactors. A certain degree of uncertainty is inherent with the laboratory experimental measurements and the derivation of the appropriate stoichiometrical and kinetic relationships. In this paper, we examine the effect of these uncertainties have on the operation of zinc pressure leach autoclaves by performing a series of simulations with the aid of a comprehensive reactor model we have previously developed and described in literature. In particular in this study, we consider the sensitivity of the autoclave operation (attainment of steady state temperature, level of zinc recovery and final acid concentration) on (i) the stoichiometry of the marmatite oxidation reaction, (with emphasis given on the impact of the iron content of marmatite and the fraction of sulphide oxidized to sulphate; (ii) the activation energy of the marmatite oxidation reaction; (iii) the constant kinetic parameter for ferrous to ferric oxidation; and (iv) the apparent equilibrium constant for ferric ion precipitation.

LIGHT WEIGHT ALLOYS FOR AEROSPACE APPLICATIONS V: Titanium Alloys

Sponsored by: Structural Materials Division, Non-Ferrous Metals Committee

Program Organizers: Eui W. Lee, Naval Air Warfare Center, Code 4342, MS5, Patuxent River, MD 20670 USA; William Frazier, Naval Air Warfare Center, Aircraft Div., Patuxent River, MD 20670-1908 USA; K. Jata, Wright-Patterson Air Force Base, WL-MLS, Dayton, OH 45433-7718 USA; Nack J. Kim, Center for Advanced Aerospace Materials, Pohang 790-330 Korea

Tuesday PM Room: 9
March 2, 1999 Location: Convention Center

Session Chair: James Fragomeni, Ohio University , Dept. of Mech. Eng., Athens, OH USA

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DEVELOPMENT OF A NEW BETA TITANIUM ALLOY (BETA-636): *Dongjian Li*[1]; Kevin J. Doherty[2]; S. J. Poon[1]; Gary J. Shiflet[2]; [1]University of Virginia, Dept. of Phys., 205 McCormick Rd., Charlosville, VA 22903 USA; [2]University of Virginia, Dept. of Mats. Sci. & Eng., Mats. Sci. Bldg., Charlottesville, VA 22903 USA

A new class of beta titanium-based alloys has been developed that possesses the desirable combination of properties of a high yield strength of up to 1650 MPa and an elongation of 10% in the aged state. After casting or solution annealing, its matrix is almost exclusively beta phase with trace amount of omega phase. No alpha phase is observed. Nanometer-sized alpha particles precipitate out from the beta matrix during aging, and grow very slowly. This, along with the homogeneous distribution of precipitates contribute to the excellent properties observed in this alloy. Further experiments are being conducted to produce ingots suitable for the industrial application of this alloy.

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OXIDATION BEHAVIOR OF TERNARY TiAl-Nb ALLOY: *Yang Li*[1]; *Ramana G. Reddy*[1]; [1]University of Alabama, Dept. of Metall. and Mats. Eng., Tuscaloosa, AL 35487 USA

The oxidation behavior of ternary TiAl-Nb alloy has been studied in pure oxygen over the temperature range of 750ϒC to 1100ϒC. The experiments were carried out using TGA. The oxidation products were analyzed using X-ray diffraction, SEM and EDS. Parabolic rate constants were calculated. An effective activation energy of 295 kJ/mol was deduced. The oxidation products were mainly a mixture of TiO2(rutile) and Al2O3 (alumina). For oxidation scale at 1000ϒC and 1100ϒC, it exhibited a layered scale of alternate rutile and alumina. The present results were also compared with that of binary TiAl.

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ENVIRONMENTAL EFFECT ON MECHANICAL PROPERTIES OF ALUMINIDE MATRIX COMPOSITES: *Masahiro Inoue*[1]; Katsuaki Suganuma[1]; Koichi Niihara[1]; [1]Osaka University, ISIR, 8-1 Mihogaoka, Ibaraki, Osaka 567-0047 Japan

Mechanical properties of nickel and iron aluminides and their matrix composites with ceramic particles and fibers were investigated in several types of environments. Ni3Al and FeAl alloys exhibits significant environmental embrittlement in air. Although the fracture properties of their matrix composites predominantly depends on the ductility at a crack tip, those are also strongly influenced by the environmental effect. The moisture induced embrittlement is a serious problem at ambient temperatures for the fracture resistance of these composites. The embrittlement phenomenon is found to be accelerated dynamically during the loading. The effect of stress applied to the specimens on the environmental embrittlement will be discussed in detail.

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EFFECT OF PROCESS VARIABLES ON THE HOT FORGE-ABILITY OF Ti-10V-2Fe-3Al ALLOY: *C. S. Lee*[1]; K S Choi[1]; D H Shin[2]; [1]Pohang University of Sci. and Technology, Center for Advanced Aerospace Mats., San 31, Hyoja-dong, Pohang 7909-784 Korea; [2]Hanyang University, Metall. and Mats. Sci., Ansan, Kyunngi-Do 425-791 Korea

Forgeability and mechanical properties of final forged products are largely dependent on various process routes. However, the detailed information on how the formability of Ti-10V-2Fe-3Al alloy is related to the initial microstructure and process variables such as temperature, strain rate etc. is not well understood. In this study it is aimed to investigate the flow characteristics of Ti1023 alloy over a range of temperature (540-840°C) and strain rate of 0.2 to 20 per s during hot compression tests and establish more reliable constitutive equation for stimulating the forging process. Constitutive equation based on the power law creep has been determined and incorporated into the commercial DEFORM program. Then the results of computer simulation have been compared with those of actual forged parts. To investigate the microstructural influence on the forgeability, microstructures containing thin and thick grain boundary alpha layers have been prepared and forged. Hot forging has been carried out above and belo w the beta transus. The optimum conditions for forging in both microstructures and process variables are discussed on the basis of present results.

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HIGH TEMPERATURE PROPERTIES OF TiB2/Ti SURFACE -ALLOYED MATERIAL FABRICATED BY HIGH ENERGY E-BEAM IRRADIATION: *Seong Hun Choo*[1]; J C Oh[1]; K Euh[1]; Sunghak Lee[1]; Yangmo Koo[1]; Nack J Kim[1]; [1]Pohang University of Science and Technology, Center for Advanced Aerospace Mats., Pohang 790-784 Korea

This study aims at improving the high temperature properties of TiB2/Ti surface alloyed materials fabricated by a high energy e-beam irradiation technique. The mixture of TiB2 powders and flux were deposited on a pure Ti substarte and a Ti10V2Fe3Al alloy substrate and then ebeam was irraditaed on these mixtures. Cracks and pores were found in the melted region of the sample processed without flux because of inhomogeneous thermal transfer. In the samples processed with a flux mixing ratio of 50% the melted region of about 1.5 mm thickness was homogeneously formed without defects and was composed of primary and eutectic TiB in the matrix. This microstructural modification including TiB greatly improved hardness especially high temperature hardness upto 450°C. These findings suggested that surface alloying using high energy e-beam irradiation was economical and usefull to the development of new advanced material with improved high temperature properties.

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OXIDATION OF ORTHORHOMBIC TITANIUM ALUMINIDE Ti22Al-25Nb IN Ai BETWEEN 650 AND 1000°C: *C. Leyens*[1]; [1]Oakridge National Lab, P.O.Box 2008, Oak Ridge, TN 37381 USA

Orthorhombic titanium aluminides are currently under investigation for aeroengine applications up to about 700°C. In some cases, orthorhombic alloys have proven superior to g-TiAl and Ti3Al based alloys with respect to fracture toughness, ductility and specific yield. Due to their low coefficient of thermal expansion and their low reactivity with SiC, orthorhombic titanium alloys are also considered as matrix material for fiber reinforced composites. The oxidation resistance of Ti22Al-25Nb, a typical orthorhombic alloy, is found to be comparable to conventional titanium alloys and Ti3Al based aluminide alloys between 650 and 800°C in air, AT 900 and 1000°C in air, the parabolic rate constant is initially on the order of that of g-TiAl based alloys, however, transition to linear growth kinetics is observed after several ten hours, resulting in poor oxidation resistance. The oxide scale contains TiO2, Al2O3 and AlNbO4 with rutile as the dominant oxide phase. Underneath the oxide scale, a nitride layer is formed. The nitride layer grows with exposure time, indicating that nitrogen diffuses through the outer oxide scale. Oxygen is enriched below the oxide scale forming an embrittled layer as wide as 300mm after 500h exposure at 900° C. The peak hardness at the outermost metal zone is up to five times higher than the bulk hardness of Ti-22Al-25Nb.

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EFFECT OF PROCESSING VARIABLES ON THE DENSIFICATION OF PIMED TiAl PARTS: *Yongchan Kim*[1]; Nack Kim[1]; Taesik Yoon[2]; S Ahn[2]; [1]Post Tech, Center For Advanced Aerospace Mats., San 31, Pohang 790-784 Korea; [2]Research Institute of Industrial Science and Technology, San 31, Pohang Korea

Very fine size of powders under 10 micron is required to achieve a near full density (>95%) of PIM(Powder Injection Molding) parts. Since the remaining pores distribute evenly throughout the PIMed part, HIPping can remove the pores completely without distorting the part shape. Therefore, PIM process can be used to manufacture a hard-to-fabricate part with a stringent material property requirement such as TiAl. In the case of the P/M processing of the alloys containing elements with a high oxygen affinity such as Ti and Al, extreme care should be taken to minimize the oxygen content in the powders and processing environment. The oxides, surface or internal, work as a diffusion barrier and cause premature halt of densification. During the thermal degradation process of organic binder, the metal powders may undergo oxidative or reducing environment. Debinding can also result in excess carbon residue depending on the process. These interstitial elements should have a significant influence on the sintering behavior of PIMed TiAl. In this study, the effect of PIM processing variables in debinding and sintering on the densification of TiAl, especially the role of interstitial elements, was investigated.

MATERIALS PROCESSING FUNDAMENTALS: Spray Forming & Thin Films

Sponsored by: Extraction & Processing Division, Process Fundamentals Committee; Jt.Extraction & Processing Division/Materials Processing and Manufacturing Division, Synthesis, Control and Analysis in Materials Processing Committee

Program Organizers: W.D. Cho, University of Utah, Dept. of Metall. Eng., Salt Lake City, UT 84112 USA; Huimin Liu, UES, Inc., Annapolis, MD 21401 USA; Srinath Viswanathan, Oak Ridge National Laboratory, P.O. Box 2008, Bldg. 4508, Oak Ridge, TN 37831-6083 USA

Tuesday PM Room: 5A
March 2, 1999 Location: Convention Center

Session Chairs: Ralph H. Zee, Auburn University, Auburn, AL 36849 USA; Huimin Liu, UES Software, Annapolis, MD 21401 USA

2:30 PM INVITED PAPER

PARTICLE MASS FLUX IN THE SPRAY CONE OF A FREE FALL ATOMIZER: *Volker Uhlenwinkel*[1]; Marko Buchholz[1]; Klaus Bauckhage[1]; [1]University of Bremen, Chem. Eng., Badgasteiner Str. 1, Bremen D-28359 Germany

The design of a free fall atomizer as well as the process parameters affect the particle mass flux distribution in the spray cone The mass flux distribution is important in spray forming because of its influence on the deposit shape and enthalpy input into the deposit. In this article the effect of different process parameters on the mass flux distribution is shown. Also different melts were atomized with the same atomizer. An empirical relation will be introduced to predict the mass flux in the spray cone. This relation will be compared with the experimental results. Finally, results of a scanning atomizer will be presented and the effect of the frequency will be discussed.

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PDA-BASED EXTENDED MODELS DESCRIBING THE MASS AND ENTHALPY FLUXES TO THE DEPOSIT AND THE PHENOMENS WITHIN THE DEPOSIT: *Klaus Bauckhage*[1]; [1]University Bremen, Chem. Eng., Badgasteiner Strabe 3, Bremen D-28359 Germany

Spray forming in some areas has become a successful alternative to conventional materials, fabrication techniques like powder metallurgy. It opens the opportunity to combine microstructural refinement (in absence of macrosegregations) with the wide flexibility in alloying and mixing as well as - under some conditions - neat net shape manufacturing with the option to produce large voluminous preforms. Spray forming means the subsequent combination of stream atomization into a wide size distribution of droplets and particle deposition on to a substrate and (furtheron) on each other, thus generating growing deposits and finally forming round billets, disks, tubes, rolls, or flat sheets without any macro- and micro-segregation. Since on the one hand spray forming has proved a good investment even under rough production conditions on the other hand growing experience under practical applications show that superheating or undercooling of the melt, mass-flow differences of the melt stream or variations of the gas pres sure May cause severe material problems of the pre-product, like coarse grain, pores of hot cracks. Thus the necessity of process control in order to avoid faults or to analyze errors in undesirable. There have been improved not only process description but also process control models and devices in order to avoid such faults of the material properties within the preform. Experimental data have been taken from representative measuring positions from inside the spray cone, helping - in comparison with the simulated date of different process modes - to describe the multiphase flow situations in the spray cone and the heat transfer conditions for the rapid cooling and partly solidifying of melt droplets before impact onto the substrate/deposit. The radial distribution of the local vertical mass flux of melt particles within the spray come for different distances from the atomizer can be described by a Gaurdian type of profile. These radial distributions differ from those profiles describing the local size distributions of the particles or the gas becomes responsible for the local enthalpy flux to the deposit. Due to the necessity of measuring and controlling the particle bound mass, momentium and enthalpy fluxes to the deposit the Phase Doppler Anemometry (PDA) has been adapted and modified in order to receive on-line and in-line data from the dynamics of the multiphase flow conditions within the spray chamber.

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DETERMINATION OF A SPLASHING THRESHOLD FOR IMPACTING METAL DROPLETS USING HIGH SPEED VIDEO IMAGING: Joachim Ulrich[1]; M. Berg[1]; *K. Bauckhage*[1]; [1]Universitat Bremem, Chem. Eng., Badgasteiner Str. 1, Bremen D-28359 Germany

Metal drops, whenever impacting with energies beyond a certain limit, create splashing. This splashing generates secondary drops - the disintergration of droplets into secondary droplets in many cases of application of spray processes is not wanted. In spray deposition processes leads to an increased overspray which reduces the yield of the process. The question is how to adjust the process parameters (e.g. drop size, drop velocity, drop temperature, target temperature in relation to the physical properties of the Mats. at those temperatures) - if possible to achieve atomization conditions leading to drop impacts with hardly any splashing. For tin, lead, copper, aluminium and steel drops experimental observations have been made using high-speed video imaging (up to 18.000 frame/sec.). The results are presented by means of non-dimensional numbers describing the fluid dynamic and heat transfer of the deposition process. An empirial found splashing threshold - described by a log-linear equation- will be presented in a double logarithmic diagram.

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EFFECT OF DEPOSITION AND POST HEAT TREATMENT ON NiTi SHAPE MEMORY ALLOY THIN FILMS: *Chen Zhang*[1]; Paul E. Thoma[2]; Ralph H Zee[1]; [1]Auburn University, 202 Ross Hall, Auburn, AL 36849 USA; [2]Johnson Controls, Inc., 1701 West Civic Dr., A37, Milwaukee, WI 53209 USA

Polycrystalline Ti-rich NiTi thin films were deposited from a single NiTi target using DC magnetron sputtering system. Free standing films were obtained by using silicon substrate. The thickness of the films was around 10-15 microns. In this investigation, the effect of different substrate temperatures during sputtering on the thin films' microstructure and transformation temperatures was examined. The influence of post heat treatment at different temperatures on the thin films' properties was also investigated. Transformation temperatures of the thin

films were measured using differential scanning calorimetry (DSC). The surface microstructure and cross sectional microstructure of the thin films were studied using a scanning electron microscope (SEM), and the crystallinity of the films was determined by X-ray diffractometry. Results show that films deposited on a hot substrate are crystalline even when the substrate temperature is as low as 300ϒC, while the normal crystallization temperature for an amorphous thin film is above 500ϒC. The microstructure of the above film has very fine grain size. The grain size increases with increasing post heat treatment temperature and increasing substrate temperature. The transformation characteristics of the films are correlated with the deposition conditions and post deposition treatment.

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ELECTRON-BEAM PHYSICAL VAPOR DEPOSITION OF MICROLAMINATE COMPOSITES: *H. L. Ludtke*[1]; G. E. Lucas[1]; C. G. Levi[2]; G. L. Bujanda[3]; J. T. Matzen[1]; [1]University of California at Santa Barbara, Dept. of Chem. Eng., Santa Barbara, CA 93106-5080 USA; [2]University of California at Santa Barbara, Mats. Dept., Santa Barbara, CA 93106 USA; [3]University of Texas at El Paso, Mats. Dept., El Paso, TX USA

Microlaminate composites were fabricated by electron-beam physical vapor deposition (EB-PVD). The laminates consisted of five 2 micron layers and were composed of either pure metal layers (Nb-Cu or Fe-Cu), or alternated between metal and intermetallic layers (Nb(Al)-Nb3Al). The metal-intermetallic microlaminates (MIMs) were synthesized in-situ by co-depositing pure Nb and pure Al, and varying the Al deposition rate to generate the layered structure. Microlaminates were examined after deposition by scanning electron microscopy (SEM), transmission electron microscopy (TEM) and energy dispersive x-ray spectroscopy (EDS). The effects of deposition rate, substrate heater temperature, and substrate material on the quality of these composites will be described.

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FABRICATION OF TIN(IV) OXIDE THIN FILM BY SOL-GEL METHOD: *Seung-Chul Lee*[1]; Jae-Ho Lee[1]; [1]Hong Ik University, Dept. of Metall. Eng. and Mats. Sci., 72-1 Sangsu-dong, Mapo-gu, Seoul 121-791 Korea

Transparent conducting tin (IV) oxide thin films have studies and developed for the electrode materials of solar cell substrate. Fabrication of tin oxide thin films by sol-gel method is process development of lower cost photovoltaic solar cell system. The research is focused on the establishment of process condition and development of precursor. The precursor solution was made of tin isopropoxide dissolved in isopropyl alcohol. The hydrolysis rate was controlled by addition of triethanolamine. Dip and spin coating technique were applied to coat tin oxide on borosilicate glass. The resistivity of the thin film was lower than 0.10-cm and the transmittance is higher than 90% in a visible range.

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REDUCTION OF CRACK PROBABILITY DURING SPRAY FORMING OF BILLETS: *Volker Uhlenwinkel*[1]; Joern Fischer[1]; Roland Schroder[2]; Stephan Hansmann[3]; Hilmar Muller[1]; [1]University Bremen, Chem. Eng., Badgasteiner Str. 1, Bremen D-28359 Germany; [2]University Bremen, Medical Eng., Badgast Str.1, Bremen D-28359 Germany; [3]Wieland Werke AG, Pruf-und Forschurgsanstat, Graf Arco Strasse, Ulm, Bayem D-89079 Germany

Cracks were observed at the top of spray formed billets for some alloys. In this paper the effect of process parameters on crack probability is discussed. After the spray rim the thermal conditions at the top of the billet change rapidly. A hot spot with melt residual can occur inside the billet and shrinkage will be suppressed due to the solidified surface of the billet. In this situation hot cracks can be initialized. The temperature history of the billet during and after the spray run is calculated. The temperature difference between core and outside diameter of the billet is taken as indicator for hot crack probability. The effect of different process parameter on the hot crack probability is discussed. The results lead to a better understanding of the process. The calculations are then as a tool to find process parameters in order to reduce or avoid hot cracks in spray formed billets.

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AVERAGING THERMAL CONDITIONS IN MOLTEN METAL SPRAYS: Dirk Bergmann[1]; Udo Fritsching[1]; *Klaus Bauckhage*[1]; [1]University Bremen, Chemical Eng., Badgasteiner Str. 1, Bremen D-28359 Germany

During the spray forming process, a continuous molten metal stream is atomized by impinging high speed inert gas jets. In the generated spray cone, the resulting metal droplets are rapidly cooled by the huge temperature difference to the surrounding gas phase and thereby partly solidified. After a certain flight and residence time inside the spray cone, the droplets impinge on the substrate and form the product (deposit). The material properties of this product depend on several process parameters and especially on the thermal state of the deposited droplets impingement. Smaller droplets cool very fast and may impinge onto the product in a completely solidified state as solid metal powder particles. Lager droplets contain a higher amount of thermal energy and impact during the state of phase change or completely liquid. It is obvious, that a certain amount of liquid content In the droplets is needed for forming the deposit. Therefore, the thermal history of metal droplets during flight in the spray cone is of great importance. To investigate this phenomena a CFD-program in combination with a solidification model, is used to describe the thermal history of individual droplets depending on their size and flight path inside the spray cone. in this solidification model the different stages like undercooling, recalescence and segregated solidification are taken into account. To describe the effects of the impinging droplet mass on the formation and heat balance of the deposit, the thermal conditions of the droplets have to be averaged at different locations. This averaging is achieved in different ways, giving differing results. The first method is the average over the droplets' total enthalpy. Which consists of the heat content and the remaining heat of fusion. The second method is the average over the heat content and the fraction solid separately. Results of these two methods show some deviations, especially at lager radial distances from the spray cone centreline, which will be discussed in terms of consolidation and energy conservation of the deposit.

MICROMECHANICS AND MICROMECHANISMS OF DEFORMATION AND FRACTURE: A SYMPOSIUM IN HONOR OF PROFESSOR ALI S. ARGON:Session IV

Sponsored by: Structural Materials Division, Mechanical Metallurgy Committee, High Temperature Alloys Committee
Program Organizers: K. Jimmy Hsia, University of Illinois, Dept. of Theor. & Appl. Mech., Urbana, IL 61801 USA; Mary Boyce, Massachusetts Institute of Technology, Dept. of Mech. Eng., Cambridge, MA 02139 USA; Tresa M. Pollock, Carnegie Mellon University, Dept. of Metall. Eng. & Mat. Sci., Pittsburgh, PA 15213 USA
Tuesday PM Room: 14B
March 2, 1999 Location: Convention Center

Session Chairs: I.-Wei Chen, University of Pennsylvania, Dept. of Mats. Sci. & Eng., Philadelphia, PA 19104-6272 USA; Anthony G. Evans, Harvard University, Div. of Applied Sci., Cambridge, MA 02138 USA

2:00 PM INVITED PAPER
CELLULAR METALS: *A. G. Evans*[1]; J. W. Hutchinson[1]; M. F. Ashby[2]; [1]Harvard University, Division of Applied Sciences, Cambridge, MA 02138 USA; [2]Cambridge University, Eng. Dept., Trumpington St., Cambridge CB2 11P2 UK

The property profile exhibited by cellular metals identifies several applications, especially in technologies requiring multifunctionality. Their specific property attributes suggest implementation as: ultralight panels/shells, energy absorbing structures and heat dissipation media as well as for vibration control. Connections between the properties that govern these performance benefits and the cellular architecture, cell morphology and density have been made. Such structural relations facilitate choices of optimum cell characteristics fordefined multifunctional application.

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MEASUREMENT OF RESIDUAL STRESSES BY INSTRUMENTED SHARP INDENTATION: *Subra Suresh*[1]; [1]Massachusetts Institute of Technology, Dept. of Mats. Sci. and Eng., 77 Massachusetts Ave., Room 13-5056, Cambridge, MA 02139 USA

A general methodology is proposed for the determination of residual stresses using instrumented sharp indentation. Invoking the invariance of contact pressure in the presence of residual stresses, or the variation of the instantaneous yield strength in the presence of a residual plastic strain in a strain-hardening material, a step-by-step method is outlined to determine pre-existing residual fields for the following three cases. (1) The elastic residual stresses are uniform over a depth beneath the indented surface which is several times larger than the indentation contact area. (2) The elastic residual stresses vary with depth beneath the indented surface. (3) Residual plastic strains of uniform values exist over a depth several times larger than the indentation contact diameter. The method proposed here can be used to estimate residual stresses and strains in such applications as thin films, coatings, or engineered surfaces whose properties are altered by such properties as ion implantation, case hardening, shot peening, laser shock peening, or machining. The predictions of the proposed method are shown to compare favorably with finite element simulations and available experimental results.

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MECHANICAL BEHAVIOR OF SOLIDS WITH LIQUID GRAIN BOUNDARIES: *Gregory J. Rodin*[1]; [1]The University of Texas at Austin, Center for Mech. of Solids Structures and Mats., 112 WRW UT, Austin, TX 78712 USA

Many engineering and geophysical materials can be described as solids with liquid grain boundaries. The mechanical behavior of such solids is quite complex and it involves many open scientific issues. Among those issues are the following: (a) The overall creep behavior and its dependence on the grain diameter. (b) Stress distribution at the grain level that controls the flow. (c) Stress distribution at the grain boundary level that controls cavitation. We will consider these issues using asymptotic estimates valid for both newtonian and non-newtonian fluids.

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THE EFFECT OF AGING ON CRITICAL TRANSFORMATION STRESS LEVELS IN SINGLE CRYSTAL Ti-50.8at%Ni DEFORMED UNDER BOTH TENSION AND COMPRESSION: Kenneth Gall[1]; *Huseyin Sehitoglu*[1]; Yuriy I. Chumlyakov[2]; Irina V. Kireeva[2]; [1]University of Illinois, Dept. of Mech. and Indust. Eng., 1206 W. Green St., Urbana, IL 61801 USA; [2]Siberian Physical and Technical Institute, Physics of Plasticity and Strength of Mats. Laboratory, Tomsk 634050 Russia

Polycrystalline NiTi that is commonly used in industrial and medical applications deforms quite differently under an applied tensile versus a compressive stress. The present research utilizes single crystal NiTi to determine the origin of tension/compression asymmetry in polycrystalline NiTi. Two different heat treatments (peak aged and over aged) and three different crystallographic orientations ([111], [110], and [100]) are utilized for the experimental study. In the over aged specimens, the asymmetry of the critical stress required to induce the transformation in tension versus compression obeys Schmid Law. For peak aged specimens, the asymmetry of the critical stress required to induce the transformation in tension versus compression is decreased, and the Schmid Law is not obeyed. The deviation from Schmid Law is accounted for by modeling the local coherent stress fields outside the precipitates in peak aged NiTi. It is also shown that polycrystalline NiTi has a strong texture of the <<111>{110} type, and the resulting deformation of polycrystalline NiTi is closely related to single crystals oriented in the [111] direction.

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3:40 PM INVITED PAPER

TWO-PHASE CERAMIC LAMINATES FROM WET DEFORMATION PROCESSING: *I-Wei Chen*[1]; [1]University of Pennsylvania, Mats. Sci. and Eng., 3231 Walnut St., Philadelphia, PA 19104-6272 USA

Laminates of structural ceramics are usually obtained by stacking up green tapes followed by hot pressing. An alternative method is by co-rolling and folding high density slurries. The exponential reduction of thickness and the exponential multiplication of layers make this process highly efficient. In addition, the different deformation resistance of the two starting slurries can be exploited to generate laminate and cellular microstructures of various spatial extent of phase connectivity. Once the long-range connectivity is lost, the sintering constraint is also relieved making pressureless firing possible. Meanwhile, a sufficiently long coherent length is still maintained to allow an extensive fracture process zone. Alumina/zirconia and other ceramic composites of very high strength and toughness have been created using this method.

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THERMAL STRESSES AND DEPOSITION PATTERNS IN LAYERED MANUFACTURING: *Alexander H. Nickel*[1]; David M. Barnett[1]; Friedrich B. Prinz[1]; [1]Stanford University, Mats. Sci. and Eng., Bldg. 550 Room 554F, Stanford, CA 94305 USA

In Layered Manufacturing objects are constructed by sequential deposition of material layers. When the deposition process involves temperature gradients, thermal stresses develop. This paper examines the effect of deposition patterns on the resulting stresses and deflections in fabricated objects. A finite element model was developed to predict the stresses and warpage for laser deposited metal parts. The resulting deflections and stresses showed a significant dependence on the deposition pattern. Experiments performed using these same deposition patterns yielded sample deflections which were in reasonable agreement with the finite element modeling predictions.

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THE MIGRATION OF GRAIN BOUNDARIES IN ALUMINUM-BICRYSTALS UNDER THE INFLUENCE OF AN EXTERNAL MECHANICAL STRESS: *Günter Gottstein*[1]; Miriam Winning[1]; [1]Aachen University of Technology (RWTH), Institute of Physical Metallurgy and Metal Physics, Kopernikusstr. 14, Aachen D-52056 Germany

The motion of grain boundaries is the key phenomenon of recrystallization and grain growth and dominates the evolution of texture and microstructure, and eventually the macroscopic physical and mechanical properties of a material. Grain boundaries are usually considered not to couple with mechanical stress owing to the lack of a long range intrinsic stress field of a grain boundary. This is certainly not true for small angle boundaries. The current study is aimed at probing the effect of a mechanical stress field on small and large angle grain boundaries. For this purpose bicrystals with <112> tilt grain boundaries and misorientation angles in a range from 4° to 21° were investigated under the influence of an external mechanical stress. The external stress used in the experiments ranged from 10-1 MPa to 10-4 MPa. In-situ measurements of grain boundary motion were conducted with an X-ray continuous tracking device. The method employed X-ray diffraction to determine the grain boundary position and, therefore, did not interfere with the grain boundary migration process itself. The mobility of the grain boundaries was measured over a wide range of temperature (250°C - 600°C) and the activation enthalpy could be determined from these measurements. It is shown, that there is an influence of a mechanical stress on grain boundary motion far beyond the commonly accepted transition between small and large angle grain boundaries. This transition from low angle to high angle grain boundaries could be identified by a conspicuous step in the activation enthalpy.

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CREEP BEHAVIOR OF Fe-C AND OTHER IRON-BASED ALLOYS AT HIGH TEMPERATURES AND HIGH STRAIN RATES: *Donald Ritchie Lesuer*[1]; Chol Kyle Syn[1]; J. D. Wittenberger[2]; O. A. Ruano[3]; M. Carsi[3]; O. D. Sherby[4]; [1]Lawrence Livermore National Lab,

Manuf. and Mats. Eng. Division, L-342, P.O. Box 808, Livermore, CA 94551 USA; [2]NASA-Lewis Research Center, Cleveland, OH 04135 USA; [3] CENIM, CSIC AV, Dept. Phys. Metall., Gregorio del Amo 8, Madrid S28040 Spain; [4]Stanford University, Dept. of Mats. Sci. and Eng., Stanford, CA 94305 USA

It is generally recognized that the time dependent plastic flow of pure metals and alloys at elevated temperature is determined by the diffusively, elastic modulus and stacking fault energy (SFE). In this paper we explore the influence of these material characteristics on the creep behavior of several steels at high strain rates. The materials studied include ultrahigh carbon steels (containing 1.2 - 1.8 %C), HSLA steel, 316 stainless steel and pure iron. A constitutive equation has been developed to describe the results with deformation involving power-law as well as power-law-breakdown behavior. Carbon was found to influence the creep rate of the steels through its influence on the diffusion coefficient and had no effect on the SFE in these materials. The substitutional solid solution alloy additions in these materials were found to produce large variations in SFE with significant influence on the resulting creep rate. The influence of these variations in diffusivity and SFE on the dominant deformation resistance will be discussed within the context of a deformation mechanism map.

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MOLECULARLY BASED NUMERICAL EVALUATION OF FREE-VOLUME IN AMORPHOUS POLYMERS: *Santosh K. Putta*[1]; Sia Nemat-Nasser[1]; [1]University of California, San Diego, Center of Excellence for Advanced Mats., 9500 Gilman Drive, La Jolla, CA 92093-0416 USA

The concept of free volume can be utilized both to study relaxation phenomenon as well as diffusion processes in polymers. Despite the lack of a clear understanding of the structure of free volume, the concept can be used as a linking factor between diffusional processes and deformation processes, which most often are coupled in polymers. A simple geometric definition of free volume, relevant for diffusion of small molecules in polymers is given, based on the molecular structure. An initial molecular structure is obtained by using a modified RIS (rotational isomeric state) approach. Then, with the aid of molecular mechanics based on minimization procedure, computationally generated molecular structures for several polymers are used to estimate free volume based on the proposed geometric definition. Numerically evaluated free-volume distributions are then compared for different types of amorphous polymers; e.g. polycarbonates and polysulfones, stressing on their relevance to the diffusion properties.

MILTON BLANDER INTERNATIONAL SYMPOSIUM ON "THERMODYNAMIC PREDICTIONS AND APPLICATIONS": Chemical Bonding and Kinetics

Sponsored by: Extraction & Processing Division, Process Fundamentals Committee, ASM International: Materials Science Critical Technology Sector, Thermodynamics & Phase Equilibria Committee
Program Organizers: Ramana Reddy, University of Alabama, Dept. of Met. & Mats. Eng., Tuscaloosa, AL 35487 USA; Dr. A. D. Pelton, Montreal, Quebec H3C3A7 Canada

Tuesday PM Room: 4
March 2, 1999 Location: Convention Center

Session Chair: John Morral, University of Connecticut, Dept. of Metall., Storrs, CT 06269-3136 USA

2:30 PM INVITED PAPER

PREDICTION OF PROPERTIES OF INTERMETALLICS USING A CHEMICAL BONDING MODEL: *Leo Brewer*[1]; [1]University of California, Berkeley, Dept. of Chem., Berkeley, CA 94720 USA

Materials with novel properties are needed for new technology developments. It is important to be able to predict which of the millions of multi-component intermetallics might provide the desired properties. A single chemical bonding model has provided reliable thermodynamic data for the metallic elements in a variety of crystal structures. (1) The model can be extended to intermetallics. An illustration of the calculations is available (2) for Al or Mg with transition metals forming intermetallics with binary CsCl structures. A number of publications will be available for similar calculations for a variety of crystal structures. The calculations will be extended to a variety of compositions and multi-component systems. The present paper will discuss the procedures that can be used to simplify the calculations and yet maintain reliable accuracy. (1) "Calculations of Thermodynamic Properties of Metastable Phases of the Elements", by John Kouvetakis and Leo Brewer. J. Phase Equilibria 14, 663-71 (1993) (2) "Calculations of the Thermodynamic Effect of the Brewer-Engel Generallized Acid-Base Reactions of 1:1 Intermetallics for Non-Transition Metals Al and Mg with Transition Metals", by Wu Hui-Fen and Leo Brewer. J. Alloys and Cmpds. 247, 1-8 (1997)

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THERMODYNAMIC STUDY OF THE ELECTRON TRANSFER IN LIQUID ALLOYS: *J. P. Bros*[1]; M. Gaune-Escard[1]; E. Hayer[2]; [1]Université de Provence I, IUSTI-CNRS UMR 6595, 5 rue Enrico Fermi, Marseille, Cedex 20 13453 France; [2]Institut fur Anorganische Chemie der Universitat Wien, Wahringerstrasse 42, Wien A-1090 Austria

By the evaluation of the results of our calorimetric measurements of many liquid binary alloys composed of a sp-metal and a transition metal, and due to the introduction of the Fermi enthalpy function with some assumptions, the concept of a transfer of electrons on alloying has been established. However, the number of electrons transferred from the sp-metal to the transition metal has been found limited for most of the alloys investigated (e.g., 2 electrons with Ni-Ga alloys for X(Ni) lower than 0.33). More and more measurements (by XPS, Cp at low temperature, resistivity) of the physical properties were recently performed on solid alloys of the mentioned type and are explained in terms of a transfer of electrons, too. The present article gives a comparison of physical and thermodynamic measurements. Summarizing, the concept of the metallic bond is discussed for these alloys.

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SIMPLE INORGANIC LIQUID GLASSFORMERS AND THE RELATION BETWEEN THEIR THERMODYNAMIC AND TRANSPORT PROPERTIES: *C. A. Angell*[1]; W. Richards[1]; K. Ito[1]; [1]Arizona State University, Dept. of Chem. and Biochemistry, Tempe, AZ 85287 USA

The factors which can affect the probability that a given liquid will fail to crystallize during cooling at moderate rates are not well understood, but usually favor liquids of complex structure. This complicates the problem of formulating analytical theories for their behavior. Fortunately there are some examples of molecularly simple systems that evidently fail to find low energy ordered packing schemes hence only become metastable at temperatures where their viscosities are already quite high. They therefore supercool more readily than would be expected at first sight. The four atom molecule S2Cl2 is one example and the even simpler (and much studied) liquid CS2, can be vitrified on addition of only small quantities of second components. In this contribution we take advantage of new and simple methods for fragility determination in liquids to discuss the behavior of these simple systems relative to that of other fragile liquids, especially molten salts. Finally we use their simple heat capacity characteristics to examine their fragilities in terms of their configuartion space densities of states.

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DIMERIZATION IN THE VAPORS OF THE RARE EARTH BROMIDES: Claus Gietmann[1]; Guido Gigli[2]; *Klaus Hilpert*[1]; [1]Research Centre Jülich, Institute for Mats. in Energy Systems, 52425 Jülich, North Rhine Westfalia Germany; [2]University of Rome, Dept. of Chem., Piazzale Aldo Moro 5, Rome, Toscana 00185 Italy

The vaporization of the rare earth bromides LnBr3 (Ln = La, Ce, Pr, Nd, Gd, Tb, Ho, Er, Tm) was investigated in the temperature range between 770 to 1040 K using Knudsen effusion mass spectrometry. The vapor species LnBr3(g) and (LnBr3)2(g) were identified in the equilibrium vapor over the different samples and their partial pressures determined. The enthalpy and entropy changes of the reactions 2 LnBr3(g) = (LnBr3)2(g) were evaluated according to the third- and second-law methods. The dimensional model by Blander and coworkers was used for the estimation of the unknown thermodynamic functions of LnBr3(g) and (LnBr3)2(g) necessary for the third law evaluation.

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THEORETICAL INVESTIGATION OF THE THERMOCHEMICAL PROPERTIES OF LITHIUM POLYMER ELECTROLYTES USED IN LITHIUM BATTERIES: *L. A. Curtiss*[1]; [1]Argonne National Laboratory, Chem. Division, 9700 S. Cass Ave., Argonne, IL 60439 USA

Ionically conducting lithium polymer electrolytes are used in lithium batteries. In this work we have used theoretical methods to study the ion-ion interactions in these systems. The structures and thermochemical properties of a series of lithium salts such as lithium perchlorate and lithium triflate have been calculated using ab initio molecular orbital theory and density functional theory. The results are used to help understand the role that they play in the conducting properties of the polymer electrolyte Mats.. In addition, the ion-polymer interactions were studied.

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ELECTROCHEMICAL BEHAVIOR OF WELDING FLUXES AND THEIR EFFECT ON WELD COMPOSITION AND MICROSTRUCTURE: *J. Ernesto Indacochea*[1]; [1]University of Illinois at Chicago, Civil and Mats. Eng. (MC246), 842 West Taylor St., Chicago, IL 60607-7023 USA

The influence of the chemical composition of the fluxes on the final chemistry of the weld metal is recognized. However, the mechanisms responsible for the transference of elements from the flux and electrode wire to the weld metal are not completely understood. In the submerged-arc welding (SAW) process, there are four phases (electrode, slag, plasma and weld pool) and five interfaces. The complexity of the system makes it difficult to apply a single model for the whole process. Attempts have been made to develop a thermodynamic equilibrium model but it has led to conflicting conclusions. In our investigation we proposed that in addition to thermochemistry, electrochemical mechanisms play an important role in the element transfer and thus, significantly influence the weld metal composition during the SAW process. In analyzing the electrochemical behavior of the SAW process, the welding wire and the workpiece become either the anode or cathode depending on the polarity used, with the molten flux and the plasm a being the electrolytes. In this presentation the role of electrochemistry, relative to other mechanisms, will be examined more directly from results on welding of alloy steels. Welding was performed by carefully selecting the flux composition and closely controlling the welding parameters. The relative importance of the electrochemical mechanism was enhanced by changing the polarity. The oxygen levels at the weld metal, droplet and electrode tip will be interpreted based on this mechanism. Also the changes in the levels of manganese in the weld metal and of manganese oxide in the slag will be explained based on thermodynamic and electrochemical mechanisms.

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THE SURFACE TENSION DRIVEN BENARD CONVECTION: A UNIVERSAL PHENOMENON: *Pierre Cerisier*[1]; [1]I.U.S.T.I. University of Provence, 5, rue Enrico Fermi, Marseille, Cedex 13 13453 France

A vertical temperature gradient is established between the lower and upper horizontal limiting surfaces of a shallow horizontal liquid layer. The upper surface is free. Beyond a critical temperature gradient the liquid is in convection. Generally the convective structure is composed of a mosaic of convective cells which form a two-dimensional (2D) hexagonal pattern. This phenomenon is considered as the canonical example for fundamental studies: instabilities, heat transfer, wave number selection, diffusion of dye in a liquid, spatio-temporal behavior, structural disorder, turbulence, temporal and spatio-temporal chaos etc. In this paper we consider four of many aspects of these studies: (1) Why a two-dimensional (2D) hexagonal structure? When can a roll or square or hexagonal structure be observed? (2) Influence of the earth's rotation on the structure. (3) Description of the regular and disordered structure. Analogies with 2D crystals. Tools to study such structures. Strong structural analogies and common properties with other 2D structures existing in minerals, metals, botany and zoology. Age of a convective structure and of a living structure. Formal analogy between the birth of a convective cell and that of a living cell. (4) The problem of surface deformation: convex, concave or "volcano"?

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LIMITATION OF THE RULE OF ADDITIVITY IN PREDICTING PHASE TRANSFORMATION DURING CONTINUOUS COOLING: *Yuntian T. Zhu*[1]; Terry C. Lowe[1]; Robert J. Asaro[2]; [1]Los Alamos National Laboratory, Mats. Sci. & Tech., MS G 755, Los Alamos, NM 87545 USA; [2]University of California at San Diego, Dept. of Applied Mech. and Eng. Sci., La Jolla, CA 92093 USA

The rule of additivity was first proposed for predicting the incubation time for nucleation of solid phases during continuous-cooling phase transformations, and has since been widely used for both the nucleation incubation and the entire process of phase transformation. While having been successfully used to calculate the transformed volume fraction during continuous cooling in many steel alloy systems, there is experimental evidence that shows rule of additivity to be invalid for describing the incubation time for nucleation. We have recently demonstrated using classical nucleation theory that the rule of additivity is invalid for the incubation time for nucleation. However, in practice, the relative error caused by using the rule of additivity could be very small in many cases due to the resolution limit of current experimental techniques. Experimental evidences and theoretical basis on the validity and limitations of the Rule of Additivity will be presented, and recommendations and cautions for its application will be given.

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HOMOGENEOUS NUCLEATION: Joseph L. Katz; Dep't. of Chemical Engineering, Johns Hopkins University, Baltimore, MD 21218 USA

Nucleation processes are very poorly understood. Often, one has no idea what constitutes a "nucleus" or what is the nucleating event. However, for vapor condensation processes, a kinetic description of homogeneous nucleation is possible. With it, one can clearly explain why nucleation occurs, and clear up significant confusion about the role of free energy and what is a critical nucleus. This approach can be generalized to cover condensation on surfaces, nucleation with simultaneous chemical reaction, and nucleation in the presence of an anti-nucleator. The limitations of these ideas and of our knowledge for bubble nucleation and for crystal nucleation also will be presented.

MINIATURE STRUCTURES & COMPONENTS UNDER CYCLIC LOADING; FATIGUE & INTERNAL FRICTION: Session II

Sponsored by: Structural Materials Division, Non-Ferrous Metals Committee; Electronic, Magnetic & Photonic Materials Division, Electronic Packaging and Interconnection Materials Committee; ASM International: Materials Science Critical Technology Sector, Flow & Fracture Committee,

Program Organizers: H. D. Merchant, Gould Electronics, Inc., Eastlake, OH 44095-4001 USA; Thomas R. Bieler, Michigan State University, Dept. of Mats. Sci. & Mech., East Lansing, MI 48824-1226 USA; James C. Earthman, University of California, Dept. of Chem. Eng. & Mats. Sci., Irvine, CA 92717-2535 USA; M. Wuttig, University of Maryland, Dept. of Mats. & Nuclear Eng., College Park, MD 20743-2115 USA

Tuesday PM Room: 11B
March 2, 1999 Location: Convention Center

Session Chair: Manfred Wuttig, University of Maryland, Dept. of Mats. and Nuclear Eng., College Park, MD 20742-2115 USA

2:00 PM INVITED PAPER

MECHANICAL PROPERTIES OF THIN-FILM MATS. EVALUATED FROM AMPLITUDE DEPENDENT INTERNAL FRICTION: *Yoichi Nishino*[1]; [1]Nagoya Institute of Technology, Dept. of Mats. Sci. and Eng., Gokiso-cho, Showa-ku, Nagoya, 466-8555 Japan

In our attempt to study the mechanical properties of thin films, we have examined the amplitude dependence of internal friction in aluminum thin films on silicon substrates. Procedures for analyzing the internal friction data are presented, firstly for evaluating the internal friction in the film separately from the measured internal friction of the composite system, and secondly for converting the internal friction in the film into the plastic strain as a function of effective stress on dislocation motion. The stress-strain responses thus obtained for aluminum films show that plastic strain of the order of 10^{-9} increases nonlinearly with increasing stress. The microflow stress at a constant level of plastic strain is inversely proportional to the film thickness, provided the grain size is larger than the film thickness. The film-thickness effect in the microplastic deformation can be associated with the bowing of dislocation segments whose ends are fixed at the film surface and at the film-substrate interface.

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THE REINFORCING EFFECT OF COVERLAYERS ON FATIGUE CRACK GROWTH IN FLEX CIRCUITS: EXPERIMENTS AND ANALYSIS: *Alan T. Zehnder*[1]; [1]Cornell University, Dept. of Theoretical and Applied Mech., Ithaca, NY 14853 USA

In numerous experiments it has been observed that the fatigue life of flex circuits, consisting typically of a thin copper layer on a flexible polyimide substrate, is greatly enhanced when the copper is sandwiched by the addition of a second polyimide layer known as a coverlayer. Through a series of fatigue crack growth experiments, and theoretical and computational fracture mechanics analyses we have shown that the increase in fatigue life can be attributed to the polyimide coverlayer bridging across cracks in copper. In this way the coverlayer provides reinforcement to the copper partially closing cracks, thus reducing the stresses at the tips of cracks in the copper. The reduction in crack tip stresses translates directly to a reduction in the rate of fatigue crack growth, hence an increase in fatigue life. That the polyimide could reinforce the copper in any significant way was at first surprising to us since the polyimide is much more compliant than the copper.

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EFFECT OF MATERIAL PROCESSING ON FATIGUE OF FPC ROLLED COPPER FOIL: *Junji Miyake*[1]; Yoshio Kurosawa[1]; Takaaki Hatano[1]; [1]Nippon Mining and Metals Company, Ltd., 10-1, Toranomon 2-Chome, Minato-Ku, Tokyo 105 Japan

The effect of cold rolling reduction and grain size at the final annealing in the rolled copper foil processing on the fatigue property of the foil were examined to attempt further fatigue property improvement. The fatigue property was characterized by the flex and fold fatigue cyclic tests. As the rolling reduction increases, more enhanced cubic texture develops after annealing for the recrystallization. Finer grain before the cold rolling was favorable for obtaining enhanced cubic texture. It is noted that the fatigue property of the foil processed depends on the fatigue cyclic mode. Enhanced cubic texture leads to higher flex fatigue property, but lower fold fatigue property. The system-relationship among materials processing variables(processing), texture evolution(microstructure) and fatigue properties(property) will be discussed.

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INTERNAL FRICTION IN SHAPE MEMORY AND GIANT MAGNETOSTRICTIVE THIN FILMS: *Manfred Wuttig*[1]; [1]University of Maryland, Dept. of Mats. and Nuclear Eng., Stadium Dr., Bldg. 090, Room 1110, College Park, MD 20742-2115 USA

'The internal friction of thin films of NiTi, NiTiPd and CuNiAl shape memory alloy (SMA) poly- and graphoepitaxially grown single crystalline as well as giant magnetostrictive alloy (GMA) Terfenol-D single layer and (approx. 10nm FeTb)/(approx. 10nm (Co)Fe) multilayer films will be reported and analyzed. The friction gives insight into the evolution of the martensitic transformation in SMA films: For substrate constrained SMAs the equilibrium microstructure develops irreversibly with changing temperature, i.e. the microstructure evolution paths for the direct and reverse transformations are different. During the reverse transformation incompatibly stressed austensite forms from the martensite phase. Therefore, a considerable shift of the temperature interval showing maximal internal friction must be expected. Experimental studies on NiTi, NiTiPd and CuNiAI films on Si substrates support the principle thermodynamic conclusions. The magneto-mechanical properties of Terfenol-D thin films and (approx. 10nm FeTb)/(approx. 10nm (Co)Fe) multilayers also show evidence of substrate constraint: a pronounced damping maximum at a magnetic field of about 1 kOe oriented perpendicular to the plane of the film is the result of a magneto-mechanical instability in the Terfenol film. The magneto-mechanical response (of rare earth amorphous/high permeability) nanosized multilayers behaves similarly.

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THE EFFECTS OF UNDERFILL ON THE RELIABILITY OF FLIP CHIP SOLDER JOINTS: P. Su[1]; Sven Rzepka[1]; *Matt Korhonen*[1]; C. Y. Li[1]; [1]Cornell University, Dept. of Mats. Sci. and Eng., Ithaca, NY 14853 USA

Thermal fatigue damage of flip chip solder joints is a serious reliability concern, although it usually remains tolerable with the flip chip connections (of smaller chips) to ceramic boards as practiced by IBM over a quarter century by now. However, the recent trend in the microelectronics packaging towards bonding large chips or ceramic modules to organic boards, means a large differential thermal expansion mismatch between the board and the chip or ceramic module. Therefore, to reduce the thermal stresses and strains at solder joints, a polymer underfill is customarily added to fill the cavity between the chip or module and the organic board. This procedure has typically resulted in an increase of the thermal fatigue life by a factor of 10, at least, as compared to the non-underfilled case. In this contribution we first discuss the effects of the underfill to reduce solder joint stresses and strains as well as underfill effects on fatigue crack propagation, as based on a finite element analysis. Secondly, we shall probe the question of the importance of the effects of underfill defects, particularly that of its delamination from the chip side, on the effectiveness of the underfill to increase thermal fatigue life. Finally, we review recent experimental evidence from ther-

mal cycling of actual flip chip modules that appears to be in full support to the predictions of our model.

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TENSION-TENSION FATIGUE OF FREE-STANDING ELECTRON-BEAM-EVAPORATED FILMS OF COPPER AND ALUMINUM: *David T. Read*[1]; [1]National Institute of Standards and Technology, Mats. Reliability Division, 325 Broadway, Boulder, CO 80303-3328 USA

Previously published results of tension-tension fatigue tests of free-standing electron-beam- evaporated films of copper and aluminum from one set of aluminum and one set of copper specimens will be described. Both films were approximately 1 μm thick. The aluminum films, tested with an earlier, manually-operated version of the test device, had significantly poorer fatigue resistance than literature results for bulk sheet material. The copper films had fatigue resistance generally within the range expected for pure bulk copper. The copper films had an apparently abrupt transition from plastic ratchetting to mainly elastic behavior at about 1000 cycles. One copper film, tested at a stress of about 0.4 times the ultimate, endured over 100,000 load cycles without failure; and, its tensile behavior after cycling was indistinguishable from unfatigued specimens. Transmission-electron-microscope observations of the copper specimens were made, and will be described. It will be argued that the lack of correlation between visible geometric defects on the specimens and crack initiation sites indicates that optically invisible microcracks are a key factor in the fatigue failure process in these specimens.

NANOSTRUCTURED HYBRID MATERIALS: Applications of Nanostructured Materials

Sponsored by: Electronic, Magnetic & Photonic Materials Division, Structural Materials Division, Chemistry & Physics of Materials Committee, Physical Metallurgy Committee

Program Organizers: Gan-Moog Chow, National University of Singapore, Dept. of Mats. Sci., Kent Ridge, Singapore 117600; Yeukuang Hwu, Institute of Physics, Academia Sinica, Nankang, Taipei Taiwan; Sara Majetich, Carnegie Mellon University, Dept. of Phys., Pittsburgh, PA 15213 USA; Luz Martinez-Miranda, University of Maryland, Dept. of Mats. & Nuclear Eng., College Park, MD 20742-2115 USA; Robert D. Shull, NIST, Bldg. 223 Rm. B152, Gaithersburg, MD 20899 USA

Tuesday PM Room: 16A
March 2, 1999 Location: Convention Center

Session Chair: Luz Martinez Miranda, University of Maryland, Dept. of Mats. and Nuclear Eng., College Park, MD 20742 USA

2:00 PM INVITED PAPER
FTIR STUDY OF A NANOCRYSTALLINE BaTiO3/CuO COMPOSITE AS NOVEL ELECTRICAL CONDUCTANCE CO2 SENSOR: *Marie Isabelle Baraton*[1]; Lhadi Merhari[2]; Patrick Keller[3]; Karina Zweiacker[3]; Uwe Meyer[3]; [1]LMCTS, Faculty of Sciences, ESA 6015 CNRS, 123 Ave. Albert Thomas, Limoges F-87060 France; [2]Ceramac, Limoges F-87060 France; [3]Fraunhofer Institute for Biomedical Eng., Sensorsystems/Microsystems/Microsystems Dept., Sankt Ingbert Germany

The response of an electronic conductance sensor toward gases is due to the variation of the free carrier concentration induced by changes in the sensor environment. This mechanism, which essentially develops at the interface, reflects the adaptability of the semiconductor surface to the modifications of the surrounding gaseous milieu. From a chemical point of view, these surface changes correspond to adsorption/desorption processes and, therefore, are controlled by the chemical composition of the sensor surface. Hence the first steps toward the improvement of the sensor characteristics (sensitivity, response time, drift ...) are dependent on the comprehension of the chemical phenomena occurring at the gas-sensor interface. Both surface chemical composition and surface reactivity must be controlled to fabricate reproducible sensors. Obviously, this is particularly critical for nanostructured materials because the increase of the specific surface area and of the grain boundary volume implies an increase of the contaminant concentration at the surface, possibly leading to adverse effects. Conversely, a significant increase of the sensitivity can be expected from nanomaterials-based sensors. Fourier transform infrared (FTIR) spectrometry has already proved to be a particularly performant tool for the surface analysis of nanosized materials. In this paper, the technique is applied to the surface study of a BaTiO3/CuO nanocomposite powder which has been successfully used to fabricate electronic conductance sensors for CO2 detection. The chemical composition and the surface reactivity of the composite nanopowder are discussed before studying the interaction of CO2 with the sensor simulated by a pressed pellet of nanopowder. Both the formation of new surface species and the variation of the pellet electrical conductivity upon CO2 adsorption are simultaneously followed in situ by FTIR spectrometry. Then, the correlation between electrical conductivity changes and surface chemical modifications are discussed. This research is supported by the European Commission in the framework of the Brite-EuramIII program (contract BRPR-CT95-0002).

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NANOSTRUCTURED GAS SENSORS: *Hong Ming Lin*[1]; [1]Tatung Institute of Technology, Mats. Eng., Tatung Institue of Technologyhmlin, Taipei 104 ROC

For certain industries, the need of monitoring specific gases, such as CO, CO2, SO2, NO2 and H2S, at the specific location is increasing. Gas sensors are getting important and in great demand recently. Metal oxide semiconductor (MOS) type gas sensor is the most popular one because of the quicker response better than other types. The traditional MOS sensors are made of thin film or the Schottky diode. Ideally, the electrical signal generated by the sensing elements is linearly proportionate to the physical changes in the environment. However, in reality, due to the special characteristics and structure of the Mats., a linearly proportional output is uncommon. Nanocrystalline materials with the particle size smaller than 100 nm exhibit many amazing properties, which are not found in conventional Mats.. One of the distinctive features, the main effect of gas sensors, is an extremely large specific surface area. When sintered into porous nanocrystalline film, it will not only retain its gas-sensing surface, but also increase its sensitivity and response efficiency to gases and also decreasing the optimal operation temperature of gas sensors. The promotion of this technology will be very helpful for the industry to develop the nanostructured gas sensors. This study will profoundly to examine the gas-sensing materials of nanostructured WO3, TiO2 and ZnO and the doping concentration effects on sensing properties of the CO, CO2, NO2 and H2S gases.

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NANOSTRUCTURED MATERIALS FOR GAS SENSORS: *Virgil Provenzano*[1]; Michel Trudeau[2]; [1]Naval Research Laboratory, Dept. of Mats. Sci. and Tech., Code 6323, 4555 Overlook Ave. SW, Washington, D.C. 20375 USA; [2]Hydro-Quebec, Emerging Technologies, 1800 Boul. Lionel-Boulet, Varennes, Quebec Canada

Nanostructured materials, with their small grain size, large number of grain boundaries and surfaces, together with their strong reactivity with gaseous species, are very interesting materials for gas-reactive applications, including gas sensors. In this paper, the basic characteristics of nanostructured materials, especially those related to gas sensors, will be reviewed. This will be followed by presenting a synopsis of recent results obtained from a joint research and development effort involving the Naval Research Laboratory and the Research Laboratory of Hydro-Quebec on nanostructured gas sensors for naval and dual-use applications. The paper will conclude by briefly considering both the challenges as well as the opportunities offered by nanostructured materials for developing the next generation of gas sensors with significantly improved properties.

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4:00 PM INVITED PAPER

NANOSTRUCTURED MATERIALS FOR THERMAL MANAGEMENT: Jackie Y. Ying[1]; *M. L. Panchula*[1]; [1]MIT, Chem. Eng., Rm 66-544, 25 Ames St., Cambridge, MA 02139 USA

Improved thermal management materials are necessary to increase the efficiency, speed, and reliability of many common devices. In some instances, such as turbine blades and other heat engine components, the material must insulate the underlying metal from the extremely high temperatures of the operating environment. In order to fulfill this protective role the material must have a low thermal conductivity, high damage tolerance, and low oxygen permeability. At the other extreme, the next generation of computer chips will be running faster, and most likely, hotter. In order to reduce the temperature of the chips and prevent premature aging and failure, the chips must be cooled by mounting them on a ceramic with high thermal conductivity, low dielectric losses, and good mechanical properties. While the requirements for the two applications described are very different, nanostructured materials may provide the answer for both cases. This talk will focus on our research on (i) Al2O3/ZrO2 nanocomposite for thermal barrier coating applications and (ii) AlN as a high thermal conductivity substrate.

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NANOSTRUCTURED MATERIALS USING ELECTROLYTIC PROCESSES: *Michel L. Trudeau*[1]; [1]Hydro Quebec, IREQ, 1800 Boul. Lionel-Boulet, Varennes, Quebec J3X 1S1 Canada

The last ten years have clearly revealed the technological potentials of nanostructured materials. However the developments in some technological fields are still in desperate need of synthesis processes that can generate large amount of fully dense nanostructured products. This is the case for instance for soft magnetic materials. It has been showed a number of years ago, that by decreasing the average crystal size of soft magnetic materials in the nanometer regime, it is possible to reduce drastically their magnetic losses. However, many studies done in recent years have demonstrated that large-scale soft magnets can not be obtained by the densification of nanostructured powders. On the other hand, a number of works have showed that by controlling the current profile during electrodeposition and through the addition of grain growth of the inhibitors, it is possible to control the nucleation and growth of the deposited materials. Dense samples, with a crystalline size as low as 5 to 7 nm, can thus be synthesized. Compared to other techniques, pulse-electrodeposition has received little attention as a synthesis method for producing large quantities of fully dense nanostructued materials. In this work we will discuss the synthesis of soft magnetic materials, in particular Fe and Fe-riched Fe-Ni alloys obtained by controlling different electropdeposition parameters. We will also present data on the synthesis of new gas sensing nanostructured materials, in which presence of atmospheric pollutants. These examples will demonstrate that electrolytic processes can be the major synthesis technique for large-scale development of dense nanostructured materials.

REACTIVE METALS: General Session II

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 USA

Tuesday PM — Room: 5B
March 2, 1999 — Location: Convention Center

Session Chairs: Renato G. Bautista, University of Nevada -- Reno, Mackay School of Mines, Dept. of Chem. and Metall. Eng., Reno, NV 89557-0136 USA; David L. Olson, Colorado Scool of Mines, Dept. of Met. and Mat. Eng., Golden, CO 80401 USA

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THE PRECIPITATION KINETICS OF MAGNESIUM CARBONATE BY USE OF POPULATION BALANCE METHOD: *Zhiang Sun*[1]; Renato G. Bautista[1]; [1]University of Nevada, Reno, Dept. of Chem. and Metall. Eng., Mackay School of Mines, Reno, Nevada 89557-0136 USA

The mathematical modeling of the precipitation process involves the kinetics of the nucleation, growth, and agglomeration of the crystal particle. In this paper, the population balance technique was used to develop the precipitation kinetics of magnesium carbonate. The experimental magnesium carbonate precipitation data from a solution of $MgCl_2$ and Na_2CO_3 reported by Devasahayram and Khangoaukar [Minerals and Metall. Processing, 12, (3), 1995, 157-160] were used in this study. The nucleation rate, B°, can be represented by the equation $B° = 1.768 \times 10^{-9} G^{0.995}$ and the linear growth rate, G, can be represented by the equation $G = -L/t \ln \{n_i/n°\}$. The kinetics is first order, indicating that the growth of the particulate is dependent on size. These results can be used to predict the behavior of continuous precipitation of magnesium carbonate, to control the particle size, and the size distribution of the precipitates.

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DUNITE (OLIVINE) AS A SOURCE OF MAGNESIUM METAL: *Kermit B. Bengtson*[1]; [1]Consultant, 7411 Chippewa Trail, Yucca Valley, CA 92284-4710 USA

Dunite (olivine) occurs as large masses at several surface locations in the world. It analyzes 49.2% MgO and 42.1% SiO_2 together with FeO, MnO, NiO, and CoO. Na_2O, K_2O, and CaO are present in only trace amounts; B and S are absent. Olivine is known to be decomposed by HCl, but under most conditions silica gel is formed, rendering economic separation of the reaction products impreactical. Leaching conditions are reported which recover 92% of the total MgO in a simple exothermic leach of a few minutes' duration as a solution containing 25% dissolved chlorides. The easily filterable silica has a BET surface area of 110 m^2/g. FeO, MnO, NiO, and CoO also dissolve during leaching. Means are described for removing these metals as filterable oxides without the addition of extraneous chemicals. The resulting pure concentrated $MgCl_2$ solution, prepared without discharge of chlorides to the environment, could provide an economically advantageous feed to the dehydration step of a chloride electrolysis for the production of Mg metal.

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RECOVERY OF PURE MnO2 FROM MEDIUM-GRADE LOCAL MANGANESE ORES: *M. B. Morsi*[1]; [1]Central Metall. Research and Development Institute, Pyrometallurgy Lab., P.O. Box 87, Helwan, Cairo Egypt

Local medium-grade manganese ore was blended with different amounts of sodium bisulphate as sulphatizing agent and roasted at temperatures up to 800°C for various periods. The roasted products were subjected to water leaching to recover the soluble manganese sulphate. Maximum recovery of manganese as soluble sulphate achieved under optimum conditions was 98.5%. The leached liquors of manganese sulphate were purified and chemically treated to obtain pure γMnO_2 suitable for dry cell batteries. The purified solution was concentrated to obtain crystallized manganese sulphate and other valuable manganese chemicals. The mechanism and kinetics of the sulphatizing roasting process were suggested.

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KINETICS OF DISSOLUTION OF MOLYBDENUM FROM SECONDARY SOURCES / SCRAPS: *Raj P. Singh*[1]; Michael J. Miller[1]; [1]OSRAM SYLVANIA Products Inc., Research and Development Division, Chem. Development Dept., Hawes St., Towanda, PA 14848 USA

This paper pertains to the kinetics of dissolution of molybdenum from secondary sources containing metallic molybdenum. According to the literature, molybdenum can be dissolved in oxidizing acidic media such as nitric acid (HNO_3) and hydrogen peroxide (H_2O_2). Therefore, two nitric acid containing media, HNO_3-HCl (aqua regia) and HNO_3-H_2SO_4 and one H_2O_2 medium were investigated for this purpose. Reaction in all solvents i.e., HNO_3-HCl, HNO_3-H_2SO_4 and H_2O_2 was of double decomposition type with first order rate kinetics. Although dissolution of only a few molybdenum sources was studied, results can be applied to all type of molybdenum metal secondary source types.

SURFACE ENGINEERING: SCIENCE AND TECHNOLOGY I: Diamond and Related Coatings

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

Program Organizers: Yip-Wah Chung, Northwestern University, Dept. of Mats. Sci. & Eng., Evanston, IL 60208 USA; Ashok Kumar, University of South Alabama, Dept. of Elect. & Comp. Eng., Mobile, AL 36688-0022 USA; John E. Smugeresky, Sandia National Labs, Livermore, CA 94551-0969 USA

Tuesday PM Room: 7B
March 2, 1999 Location: Convention Center

Session Chairs: Jeffrey S. Zabinski, AFRL/MLBT, Nonstructural Mats. Branch, Wright-Patterson AFB, OH 45433-7750 USA; G. Radhakrishnan, The Aerospace Corporation, Mech. and Mats. Tech. Center, Los Angeles, CA USA

2:00 PM INVITED PAPER

DIAMOND AND DIAMOND-LIKE COMPOSITE COATINGS: *J. Narayan*[1]; R. Q. Wei[1]; V. Godbole[1]; A. K. Sharma[1]; [1]North Carolina State University, Dept. of Mats. Sci. and Eng., Raleigh, NC 27695-7916 USA

We have improved adhesion and wear of diamond and diamond-like coatings by reducing internal stresses in the films and providing appropriate buffer layers between the film and the substrate. Discontinuous layers of diamond are coated with layers of titanium carbide and aluminum nitride to manage local stresses within the diamond composite films. The adhesion of diamond layers can be improved by providing appropriate interposing layers, which promote strong bonding and graphitization. For diamond-like films, doping with appropriate elements reduces internal stresses and effects mechanical properties to produce functionally gradient Mats.. The adhesion in diamond-like films has also been improved via a buffer layer approach. The structural and medical applications of these novel structures are discussed.

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DEPOSITION, CHARACTERIZATION, AND APPLICATIONS OF METAL-CONTAINING, DIAMOND-LIKE CARBON FILMS: *Gary L. Doll*[1]; [1]Timken Research, Mats. Sci. Dept., Canton, OH 44706 and North Carolina State University, Dept. of Mats. Sci. and Eng., Raleigh, NC 27695 USA

Metal-containing diamond-like carbon films can be deposited by DC magnetron sputtering of metals such as titanium, tantalum, or tungsten in a partial atmosphere of argon and a hydrocarbon gas. Films deposited by this technique can be done so at substrate temperatures well below 150ϒC, making them attractive tribological coatings for case carburized steel components. The physical, mechanical, and tribological properties of these coatings are strongly dependent on the deposition conditions. Characterization experiments used in the development of these films are examined, and sever applications where metal-containing diamond-like carbon films are used as tribological coatings are reviewed.

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STRUCTURAL STUDY AND MECHANISMS OF NUCLEATION AND GROWTH OF DIAMOND CRYSTAL GROWN ON SCRATCHED Si(100) SUBSTRATES BY HOT FILAMENT CHEMICAL VAPOR DEPOSITION METHOD: *M. Shamsuzzoha*[1] and Ashok Kumar[2], [1]Department of Metallurgical and Materials Engineering, The University of Alabama, Tuscaloosa, AL 35487; [2]Department of Electrical Engineering, University of South Alabama, Mobile, AL 36688

CVD diamond films deposited on intentionally scratched Si(100) substrates, both free and containing seeded diamond crystals, have been investigated by x-ray diffraction and transmission electron microscopy techniques. Films grown on substrates scratched by a diamond paste and containing seeded diamond crystals appear to distribute on the substrate well and show little evidence of any existing void in the microstructure. The film microstructure is comprised of sparsely populated diamond crystals of faceted morphology embedded in the matrix of graphite and amorphous carbon. Substrates scratched either by diamond paste or by an abrading tool, but containing no seeded crystal, develops a film with a high density of diamond particle and a lower concentration of graphite and amorphous carbon. Diamond particles found in these two types of substrate show difference in their crystal morphology; exhibiting faceted crystal morphology on substrates treated with abrading tool and complex crystal morphology, with ragged surfaces on substrate treated with diamond paste. A distinctive feature found common to diamond of either crystals morphology is the appearances of a zigzag network of constituent twins. The observed structural features of grown diamond crystals are explained on the basis of an existing nucleation and growth mechanism suggested for the freezing of diamond cubic crystals from melt.

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A COMPARISON OF THE CVD DIAMOND NUCLEATION AND GROWTH PROCESSES ON MONOCRSTALLINE COPPER AND SILICON: *J. C. Arnault*[1]; L. Demuynck[1]; L. Constant[1]; C. Speisser[1]; F. Le Normand[1]; [1]Instut de Physique et Chimie de Strasbourg, Groue Surfaces-Interfaces, IPCMS-GSI, UMR 46, Bat 69, 23, Rue du ess, Straabourg 67037 France

CVD diamond synthesis is now well established. However, main diamond applications require a better control of the nucleation and growth mechanisms. At the early states, there is a strong competition between diamond nucleation and carbon phases formation (carbide, graphite, DLC). We will show that the nucleation, studied by electron spectroscopies, SEM, HRTEM and AFM, is quite very different depending on the substrate. On silicon surfaces, a carbide layer of 1-2 nm thick is formed within the first minutes of deposition (1). Furthermore, an etching process by the radical hydrogen occurs, including surface defects, possible preferential sites for the diamond nucleation (2). The part of controlled defects in the nucleation mechanism will be illustrated. On copper, where no carbon miscibility occurs, oriented turbostratic graphite layers are stabilized during the early stages of deposition (3). Some of them are quite new (oignons, polyhedral graphite). (1) F. Le Normand, J. C. Arnault, V. Parasote, L. Fayette, B. Marcus and M. Mermoux, J. Appl. Phys. 80 (3), 1830 (1996); (2) J. C. Arnault, S. Hubert and F. Le Normand, J. Phys. Chem. B 102, 4856 (1998); (3) L. Constant, C. Speisser and F. Le Normand, surf. Sci. 387, 28 (1997)

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THE FORMATION OF SiC INTERFACE AND ITS EFFECTS ON DIAMOND NUCLEATION: *S. T. Lee*[1]; I. Bello[1]; [1]University of Hong Kong, Dept. of Phys. and Mats. Sci., Center of Super-Diamond and Advanced Films, Hong Kong

Three different techniques, namely, bias-enhanced nucleation, ECR-enhanced nucleation and direct ion beam deposition, were employed to enhance diamond nucleation on mirror-polished silicon substrates. It was observed that a SiC layer formed prior to the diamond nucleation by all three nucleation methods. The formation and characteristics of this SiC interface was investigated by high-resolution TEM, selected-area diffraction, and micro-Raman spectroscopy. A theoretical model of diamond/SiC/Si interfacial structure was established with the molecular orbital theory and molecular mechanics/dynamics simulations. The interaction of reactant radicals in the plasma with the substrate surface and the effects of SiC formation on diamond nucleation are discussed.

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RECENT STUDIES ON THE ELECTRON FIELD EMISSION CHARACTERISTICS OF DIAMOND AND DIAMONDLIKE CARBON EMITTERS: H. F. Cheng[1]; I. N. Lin[1]; C. T. Hu[1]; C. Y. Sun[1]; M. Yokoyama[1]

Diamond-like-carbon (DLC) films synthesized by pulsed laser deposition process can be turned-on at low applied field and exhibit large electron field emission capacity, showing great potential for the appli-

cations as electron emitters. The substrate temperature used for preparing the diamond-like carbon (DLC) films by the pulsed laser deposition process pronouncedly modifies the sp3-bonds content and morphology of the DLC films. large proportion of sp3-bonds results in high emission current density (J_e), whereas spherical geometry of the clusters induced low turn-on field (E_0). By contrast, the Au-precoatings reduced the resistance for the electron to transport from the substrate to the DLC clusters without modifying the nature of the DLC clusters. The incorporation of boron-species into the DLC clusters further improved their electron field emission properties via the induction of impurity energy levels Moreover, the post-annealing and the (Ar, N_2 or O_2) post-treatment processes alter the morphology and the proportion of sp3-bonds for the DLC films, resulting in marked improvement on their electron field emission behavior.

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A FINITE ELEMENT MODELING OF THERMAL RESIDUAL STRESSES DURING BRAZING OF DIAMOND TO TUNGSTEN CARBIDES: *R. Torres*[1]; [1]Colorado School of Mines, Dept. of Metall. and Mats. Eng., Advanced Coatings and Surfaces Eng. Laboratory (ACSEL, Golden, CO 80401-1887 USA

The use of polycrystalline diamonds for shear bits used in rock drilling has been expanding rapidly in recent years. These diamond bits are brazed to tungsten carbide using an alloy filler material at high temperatures. During cool down from the braze temperature, the diamond-tungsten carbide joint develops residual stresses. The origin of the stresses is due to the mismatch between the coefficient of thermal expansion, Young's modulus, and Poisson's ratio of the two components involved. Depending on the magnitude and sign of these stresses, delamination or debonding of the joint may occur; or failure may occur either in the diamond or the tungsten carbide piece. The purpose of this investigation is to calculate the thermal residual stresses developed in these joints using a finite element model. Modeling was conducted by independently varying the temperature from which the joint was cooled down (850 to 1150ϒC), the thickness of the braze layer (25 to 150 microns thick), and the diameters of the diamond and tungsten carbide samples (5.2 to 19 mm). The shear, axial, and radial stresses were computed. It was observed that lower brazing temperatures minimize the thermal stresses and also minimize the risk of graphitization of diamond. It was also noted that the thicker the braze layer the greater is the stress relaxation, and maximum relaxation occurred when the braze layer deformed plastically. Optimum parameters for brazing are being developed for a given filler material.

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ADHESION AND WETTING IN DIAMOND AND CARBIDE SYSTEMS: *S. V. Yulyugin*[1]; [1]Institute for Mats. Sci. Problems of National Academy of Sci., 3 Krzhyzhanovsky Str., Kyiv 252142 Ukraine

The common fundamental conformity to natural laws of adhesion and wetting of diamond by liquid metals has been confirmed. These data have been compared with dependencies on adhesion and wetting of carbides. It has been found that high adhesion and wetting of solids by melts is determined mainly by chemical interface interaction. The measurements of the contact angles and adhesion of liquid metals have been complemented by the estimation of the value mechanical strength of metal-solid contact and data of chemical structure of the interface. Experimental studies of liquid sintering of powder composites diamond/melt and diamond//TiC/melt were carried out. The influence of some factors such as the powder granularity, chemical composition and wetting of Cu/Sn/Ti melts and other capillarity characteristics has been studied.

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THE EFFECT OF SURFACE MODIFICATION Al OR Ti FILM ON BOND STRENGTH OF JOINING AIN TO METALS: *Wladyslaw Wlosinki*[1]; [1]Warsaw University of Technology, 85 Narbutta, Warsaw 02-524 Poland

The process conditions, microstructures, reaction products and residual stress as well as their effects on the bond strength of joining surface modified aluminum nitride (AlN) ceramic to metals were studied. Radio frequency sputtering was applied to deposit surface modification aluminum or titanium film on AlN ceramic. Brazing with AgCu19.5Ti3In5 filler and diffusion bonding processes were investigated to join the different surface modified AlN ceramics to Cu and FeNi4 metals. The strength of the joints was improved because the interfacial Al or Ti film improved the wettability of AlN. The maximum bond strength of 127 MPa and 176 MPa could be obtained for brazing surface modified AlN to Cu and to FeNi42 respectively at 1173K for 20 min. And the bond strength of diffusion bonding AlN to Cu joint could be improved further with a functional gradient material(FGM) interlayer coated using plasma spraying.

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STRUCTURE AND PROPERTIES OF PVD-COATINGS BY MEANS OF IMPACT TESTER: Techn. E. Lugscheider, Univ.-Prof. Dr. techn. O. Knotek, Dipl.-Ing. Christian Wolff, Dipl.-Ing. Stephan Berwulf, Materials Science Institute-Aachen University of Technology, RWTH-Aachen, WW, Augustinerbach 4-22, 52062 Aachen, Germany

Machine parts like rolling bearings or gears are stressed during operation in a changing mechanical strain. This causes wear by impacts and wear by rolling which is marked by the so called surface ruin. The appearance of surface fatigue is based upon structural transformation, cracking and cracking-growth processes and ends with the separation of debris particles caused by the above mentioned permanent changing strain . The final stage, which is equivalent to the component failure, is the so called pitting on the technical surface, which is characteristically named surface fatigue. The impact tester is used for detailed research about failure mechanisms of thin films. Statements about the adherence of hard material coatings under dynamic compressive stress can be made using this test method, due to the possibility to simulate some effects of rolling strain. Therefore a hard metal ball strikes with a frequency of up to 50 Hz onto the surface. The altitude stress can be varied to get a detailed evaluation of fatigue strength under reversal strain. Selected hard material coatings were analyzed after testing with the described method applying an impact force of 300 N, 500 N and 700 N. In the framework of this presentation MSIP (Magnetron-Sputter-Ion-Plating) coatings on titanium- and chromium basis were used. The fatigue defects and the results of this study will be discussed depending on structure and morphology of thin films.

SYNTHESIS OF LIGHTWEIGHT METALS III: Titanium - II

Sponsored by: Light Metals Division, Aluminum Committee; Structural Materials Division, Titanium Committee; ASM International: Materials Science Critical Technology Sector, Materials Synthesis & Processing Committee

Program Organizers: F. H. (Sam) Froes, University of Idaho, IMAP-Mines Bldg. #321, Moscow, ID 83844-3026 USA; C.M. Ward Close, DERA Farnborough, Struct. Mats. Ctr., Farnborough, Hampshire GUI14OLX UK; D. Eliezer, Ben Gurion University, Dept. of Mats. Eng., Neqev Israel; P. M. McCormick, University of Western Australia, Res. Ctr for Adv. Min. & Mats. Proc., Nedlands, W.A. 6907 Australia

Tuesday PM Room: 10
March 2, 1999 Location: Convention Center

Session Chairs: C. G. Li, Beijing Institute of Aeronautical Materials (BIAM), Beijing, 100095 China; Oleg Senkov, University of Idaho, IMAP, Moscow, ID 83844-3026 USA

2:00 PM INVITED PAPER

RECENT TITANIUM DEVELOPMENTS - PART I: *Rod Boyer*[1]; Oleg N. Senkov[2]; F.H. (Sam) Froes[2]; [1]Boeing Mats. Technology, P.O. Box 3707, M/S 73-43, Seattle, WA 98124 USA; [2]University of Idaho, IMAP, Mines Bldg., Rm. 321, Moscow, ID 83844-3026 USA

Traditionally the majority of titanium used in the USA has been in aerospace applications. However, after "peace broke out" in the world there has been a move to expand non-aerospace use of titanium and its alloys. Recent developments will be discussed including low cost titanium advances.

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RECENT TITANIUM DEVELOPMENTS - PART II : *Rod Boyer*[1]; Oleg N. Senkov[2]; F.H. (Sam) Froes[2]; [1]Boeing Mats. Technology, P.O. Box 3707, M/S 73-43, Seattle, WA 98124 USA; [2]University of Idaho, IMAP, Mines Bldg., Rm. 321, Moscow, ID 83844-3026 USA

Traditionally the majority of titanium used in the USA has been in aerospace applications. However, after "peace broke out" in the world there has been a move to expand non-aerospace use of titanium and its alloys. Recent developments will be discussed including low cost titanium advances.

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EXTENSION OF SOLID SOLUBILITY OF Mg IN Ti BY MECHANICAL ALLOYING: *D. Carl Powell*[1]; E.G. Baburaj[2]; F.H. (Sam) Froes[2]; [1](present address) Lockheed-Martin Skunk Works, Mechanical Test Lab, B/633 P/10, 1011 Lockheed Way, Palmdale, CA 93599 USA; [2]University of Idaho, IMAP, Mines Bldg., Rm. 321, Moscow, ID 83844-3026 USA

The light weight elements Li, Be, B, Mg, Al, Si, Ca and Sc are the potential alloying components for reducing the density of Ti. Consideration of atomic size, electronegativity and crystal structure of alloying elements, along with material cost suggests Mg as the suitable alloying element for the production of low density Ti alloys. However, alloying Mg with Ti by conventional melting routes is not feasible, since Mg boils, before Ti melts. Therefore, the synthesis of this alloy necessitates the application of non-conventional methods of alloying. In the present study, mechanical alloying has been employed to extent the solid solubility of Mg in Ti. Mechanical milling of the blended elemental powders, using a Spex 8000 mill, showed extension of solid solubility of Mg up to 24 at%. Solubility has been estimated on the basis of changes in lattice parameters of Ti. Contamination by oxygen and nitrogen also increases the lattice parameter of Ti and this effect has been taken into account. The Ti-Mg alloys formed by MA has been consolidated by HIP'ing. Electron microscopic examination of the HIP'ed samples revealed a fine a distribution of Mg particles, in the size range of 10-50 nm, in Ti matrix.

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SYNTHESIS OF COPPER BASE Cu-Ti BINARY ALLOYS BY MECHANOCHEMICAL PROCESSING: *Swati Ghosh*[1]; E.G. Baburaj[1]; F.H. (Sam) Froes[1]; [1]University of Idaho, IMAP, Mines Bldg., Rm. 321, Moscow, ID 83844-3026 USA

Copper base Cu-Ti alloys have mechanical and electrical properties comparable to those of the precipitation hardenable Cu-Be alloys. Cost effective production of Cu-Ti alloys has the potential to substitute Cu-Be alloys. Present work is an attempt to produce Cu-Ti alloys by mechanochemical processing which involves co-reduction of the $CuCl_2$ and $TiCl_4$ using CaH_2 and Mg at ambient temperatures. The reduction reaction results in the formation of Cu-Ti alloys in a matrix of $CaCl_2$-$MgCl_2$ salt mixture. The salts are leached out to obtain the alloys in the form of fine powder, in a size range of 10 - 500nm. Three copper base alloys containing 2.5, 4.7 and 11.0 % Ti have been synthesized by this process. Detailed examination of the reaction products revealed uniform powder mixtures containing Cu_4Ti and Cu-Ti solid solution. The volume fraction of the intermetallic compound has been found to increase in proportion to the Ti content.

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SYNTHESIS OF Ti-Al INTERMETALLICS BY MECHANOCHEMICAL PROCESSING: *Swati Ghosh*[1]; Dwight Linch[1]; E.G. Baburaj[1]; F.H. (Sam) Froes[1]; [1]University of Idaho, IMAP, Mines Bldg., Rm. 321, Moscow, ID 83844-3026 USA

Among the light weight intermetallics, Ti_3Al and TiAl are potential candidates for applications in aerospace systems and automobiles because of their low density and high temperature strength properties. In spite of the combination of excellent properties, the use of these intermetallics is limited because of the poor ductility and high cost. Ductility of these alloys is known to increase when the grain size is reduced to nanoscale range. It is difficult to achieve the goals of either fine grain size or the low cost of production of Ti-Al alloys by conventional methods of alloy production. The present work is aimed at the synthesis of Ti-Al intermetallics in the ultrafine powder form and at low cost, by mechanochemical processing. The process involves the co-reduction of chlorides of titanium and aluminum by CaH_2 and Mg by mechanical alloying of the chemicals to induce the reduction reaction resulting in the formation of Ti-Al intermetallics. The use of CaH_2 for the reduction reaction leads to the formation of hydrided intermetallic compounds, Ti_3Al and TiAl. Electron microscopic examination of the intermetallics reveals faceted crystals in the size range of 10 to 300 nm. Further work on consolidation of the alloy powders is in progress.

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DEVELOPMENT AND CHARACTERIZATION OF A TiAl/Ti5Si3 COMPOSITE WITH A SUBMICROCRYSTALLINE STRUCTURE: *O. N. Senkov*[1]; M. Cavusoglu[1]; G. Popescu[2]; M.L. Ovecoglu[3]; F.H. (Sam) Froes[1]; [1]University of Idaho, IMAP, Mines Bldg., Rm. 321, Moscow, ID 83844-3026 USA; [2]Polytechnic University, Dept. of Non-ferrous Metals and Alloys, 313 Independentei Splai, Bucharest, . R - 77206 Romania; [3]Istanbul Technical University, Dept. of Metall. Eng., Faculty of Chem. Metall., Maslak Istanbul, 80626 Turkey

A Ti-47Al-3Cr/Ti_5Si_3 composite with a submicrocrystalline structure was produced by mechanical alloying, thermal treatment and hot isostatic pressing. Blends of elemental and pre-alloyed powders were used for mechanical alloying. Phase reactions and microstructure stability in the mechanically alloyed powders and hot isostatically pressed compacts were studied during heating with the use of DTA, XRD, and TEM. As produced composite consisted of a homogeneously distributed mixture of gamma-TiAl and Ti_5Si_3 grains. The average grain size increased when the hot-isostatic-pressing temperature increased and it was about 200 nm after processing at 1050ϒC. During annealing at 1100ϒC for up to 500h, slow grain growth occurred, however the microstructure of the composite was much more stable than the microstructure of the Ti-47Al-3Cr alloy produced by using identical conditions. Even after annealing for 500 hours, the grains were less than 1 μm in size. Microhardness measurements were also performed which showed high hardness of this material after compaction as well as following annealing.

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SYNTHESIS OF A LOW DENSITY Ti-Mg-Si ALLOY: *O. N. Senkov*[1]; M. Cavusoglu[1]; F.H. (Sam) Froes[1]; [1]University of Idaho, IMAP, Mines Bldg., Rm. 321, Moscow, ID 83844-3026 USA

A low density titanium alloy was synthesized from blended elemental powders of Ti, Mg, and Si by mechanical alloying and heating. In some experiments a titanium hydride was used instead of titanium. Phase transformations which occurred in the system during heating were studied with the use of DTA and XRD. The powder annealing was performed in the DTA unit in an argon atmosphere. It was found that during heating of the blended powders some silicon went into solid solution in titanium while most of it exothermically reacted with magnesium at about 500ϒC producing an intermediate phase Mg_2Si. This phase was stable in titanium until the temperature of 950ϒC where it began to decompose into Mg_2Si and liquid Si, and a reaction of the silicon with titanium occurred by formation of a Ti_5Si_3 phase. The third reaction in the system was detected at about 1100ϒC and was due to formation of MgO, so that after annealing at 1100ϒC three stable phases, Ti(Si), Ti_5Si_3, and MgO, were present in the alloy. No decomposition of Ti_5Si_3 phase and formation of Mg_2Si were detected during subsequent cooling and second heating of the alloy. Essentially different phase reactions occurred in the mechanically alloyed powders. The Mg_2Si phase was already formed after heating at 450ϒC, and Ti_5Si_3 phase was detected after heating at 570ϒC. The Mg_2Si decomposed completely at a temperature of 650ϒC with the formation of MgO and Ti_5Si_3. After heating to 1100ϒC, three stable phases, $TiN_{0.3}$, Ti_5Si_3, and MgO, were present in the alloy. A discussion of the results is given.

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CHARACTERIZATION OF A REFRACTORY Ti-Al-Si ALLOY POWDER: *Y. Lytvinenko*[1]; L.D. Kulak[1]; S.A. Firstov[1]; J. Qazi[2]; O.N. Senkov[2]; F.H. (Sam) Froes[2]; [1]Ukrainian Academy of Sci., Institute for Problems of Mats. Sciences, 3 Krzhizhanovsky St., Kiev 252680 Ukraine; [2]University of Idaho, IMAP, Mines Bldg., Rm. 321, Moscow, ID 83844-3026 USA

A novel refractory powdered alloy produced by plasma rotating electrode process (PREP) in the Institute for Problems of Mats. Sci. was characterized. The main composition of the alloy was Ti-6Si-5Al-7Zr (wt.%) and a specific density of 4.6 g/cm^3. The powder particles were spherical in shape with a very small variation in size (the average particle size was about 0.35 mm). They had a dendrite microstructure and consisted of three phases, i.e. disordered alpha-Ti, ordered Ti_3Al and ordered Ti_5Si_3. The Ti_5Si_3 phase was stable during heating up to 1100ϒC while disordering of the Ti_3Al phase occurred near 1000ϒC. Oxidation resistance of the alloy was much superior to conventional titanium alloys and similar to that of a silicon nitride ceramic at temperatures up to 950ϒC. Tensile properties of ingots produced from the alloy were studied at temperatures of 20ϒC to 800ϒC. It was shown that the yield strength and tensile strength of the alloy were higher than those of a gamma-TiAl-based alloy. The fracture toughness of the alloy was about 17-20 MPavm within a temperature range of 20ϒC to 600ϒC. The results showed that the alloy could be potentially used in high-temperature (up to 800ϒC) engine applications.

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FABRICATION OF ADVANCED METAL AND INTERMETALLIC MATRIX COMPOSITES BY CONCURRENT FIBRE WINDING AND LOW PRESSURE PLASMA SPRAYING: *Kyeong Ho Baik*[1]; Patrick S. Grant[1]; Brian Cantor[1]; [1]University of Oxford, Dept. of Mats., Oxford Centre for Advanced Mats. and Composites, Parks Rd., Oxford OX1 3PH UK

A concurrent fibre winding and low pressure plasma spraying process has been developed to manufacture multi-ply fibre reinforced metal and intermetallic matrix composites in a single spraying operation. In this study, Sigma 1140+ SiC fibre reinforced Al, Ti and $MoSi_2$ composites have been manufactured using optimum plasma spraying conditions and evaluated in terms of fibre distribution, matrix/fibre cracking and fibre damage. Fibre breakage occurred during powder spraying because of an increase in fibre axial tensile stress which was caused by the difference of coefficient of thermal expansion between the matrix and the fibre. A reduction in fibre winding tension inhibited fibre breakage, but a significant fibre displacement was observed below fibre winding tension of 10 N. Fibre distribution was mainly affected by surface roughness of predeposit and a close fibre spacing gave rise to interface cracking in SiC/Ti composite and matrix cracking in SiC/$MoSi_2$ composite during secondary consolidation. It was found that the surface roughness was determined by unmelted powder particles and a fine powder spraying was favoured for uniform fibre spacing. However, Ti matrix composite using fine powder (20~50 μm) had poor mechanical properties because of oxidation embrittlement. A reduction of surface roughness was also achieved using low pressure surface rolling during powder spraying and subsequent consolidation. Surface flaws were observed on fibre coating, which degraded tensile strength. The SiC fibres extracted from Ti matrix composites had a large reduction in tensile strength compared with those extracted from Al matrix composites.

THE MARTIN E. GLICKSMAN SYMPOSIUM ON SOLIDIFICATION AND CRYSTAL GROWTH: Crystal Growth

Sponsored by: Materials Processing and Manufacturing Division, Solidification Committee

Program Organizers: Dr. N. B. Singh, Northrop Grumman Corporation, Pittsburgh, PA 15235 USA; Dr. Steven P. Marsh, Naval Research Laboratory, Code 6325, Washington, D.C. 20375 USA; Krishna Rajan, Rensselaer Polytechnic Inst., Dept. of Mats. Sci & Eng., Troy, NY 12180-3590 USA; Prof. Peter W. Voorhees, Northwestern University, Dept. of Mat. Sci. & Eng., Evanston, IL 60208 USA

Tuesday PM — Room: 11A
March 2, 1999 — Location: Convention Center

Session Chairs: Richard H. Hopkins, Northrop Grumman, STC-ESSD, Pittsburgh, PA 15235 USA; Rose Scripa, University of Alabama at Birmingham, Dept. of Mats. and Mech., Birmingham, AL 35294 USA; Krishna Rajan, R.P.I., Troy, NY 12180 USA

2:00 PM INTRODUCTION

2:15 PM INVITED PAPER
PHASE FIELD MODELING OF DENDRITIC GROWTH: *Robert F. Sekerka*[1]; Stanislav Pavlik[1]; [1]Carnegie Mellon University, Dept. of Phys. and Math., Pittsburgh, PA 15213 USA

This talk will focus on modeling of dendritic growth by the phase field model. The model is based on an entropy functional that is the integral of a entropy density assumed to be a function of energy density and a phase field variable (order parameter). The entropy density is that for a homogeneous phase, augmented by a "gradient entropy" correction. By assuming that the local rate of entropy production is positive (local form of second law) subject to the constraints of conservation, we obtain self-consistent coupled linear constitutive laws constitutive laws for energy flux and for phase field evolution. We review the results of dendrites computed from this model at large supercoolings, with emphasis on scaling laws and dendrite morphologies. At large supercoolings, dendrite shapes are found to be more nearly hyperboloidal than paraboloidal. We discuss the modification of the phase field equations needed to account for fluctuations and noise, and the influence of such fluctuations on dendrite sidebranching. This work is supported by the National Sci. Foundation under grant DMR 9634056.

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CSK-1C, TITUS AND ADVANCED TITUS FACILITIES FOR MATS. EXPERIMENTS IN SPACE: *Cestmir Barta*[1]; [1]BBT-Mats. Processing, Doubicka 11, 184 00 Prague 8, Prague Czech Republic

There are described and compared three generations of special facilities for a variety of materials experiments both on Earth and in Space. CSK-1C facility (first generation) was developed in BBT-Mats. Processing Company (BBT) and it is still operational on board MIR Orbital Station for more than 10 years. TITUS facility (second generation) was developed by BBT in cooperation with the Humboldt University (HU) in Berlin for ESA and is also operational on board MIR. Advanced TITUS facility (third generation) is being developed by BBT and HU for the German Aerospace Establishment - Microgravity Users Support Centre (DLR-MUSC) for the International Space Station (ISS Alpha). Advanced TITUS Facility represents a new conception of the space facility based on the "TITUS" currently operational on board MIR and using our experience with CSK-1C facility. It is equipped with a multizone furnace which is expected to be used for metallurgy experiments, glass processing, sublimation techniques, chemical vapour transport, solidification of melts, alloys and glasses, directional solidification of melts,

Bridgeman crystal growth, zone rafination, experiments of undercooling, thermophysical properties measurements (DTA, calorimetry), travelling heater methods, fluid physics, etc.

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ON THE MORPHOLOGY OF A SOLIDIFYING FRONT NEAR AN INSOLUBLE SPHERICAL PARTICLE: *Layachi Hadji*[1]; [1]University of Alabama, Dept. of Mathematics, 345 Gordon Palmer Hall, Box 870350, Tuscaloosa, AL 35487-0350 USA

During the unidirectional solidification of a pure substance, the presence in the melt of an inclusion is known to induce local deformations in the solid-liquid interface. In this work, the interaction between an insoluble spherical particle and a solidifying front is investigated by means of an asymptotic analysis using the width of the gap between the particle and the interface as a small parameter. An axisymmetric model is considered which accounts for (1) the thermal conductivities of the melt and the particle, (2) the disjoining pressure in the thin melt film that is sandwiched between the particle and the moving front and (3) the hydrostatic pressure in the film. An evolution equation for the deformed front is derived whose solution yields a steady state equation for the interfacial shape. The dependence of this solution, which is valid only locally, on the factors listed above is investigated. A linear stability analysis is also undertaken to isolate the stable morphology.

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DENSITY AND DISTRIBUTION OF POROSITY IN ALUMINUM ALLOYS: *C. J. Paradies*[1]; J. Wolla[2]; [1]Northrop Grumman, AS&T, M/S A01-26, Bethpage, NY 11731 USA; [2]Naval Research Laboratory, Code 6323, Bldg. 42, 4555 Overlook Ave., SW, Washington, D.C. 20375 USA

Hydrogen was intentionally introduced into several different aluminum alloys to evaluate the size, shape, density and distribution of the resulting hydrogen porosity that developed during solidification. Directional solidification experiments were performed to reveal the effect of processing conditions on the pore formation. The final pore size appears to be defined by the hydrostatic pressure and the hydrogen concentration in the melt. Bubbles nucleate at heterogeneous sites and grow by diffusion of hydrogen from the melt to the bubbles. The shape and distribution of the resulting pores depends upon both the microstructure of the solid and the time and location that the bubble nucleated within the solid structure. The density of pores probably depended upon a combination of factors including the density of nucleation sites, the local supersaturation, the local solidification time and the number of bubbles that found their way to a free surface. The results of the experiments are analyzed and discussed.

3:45 PM BREAK

4:05 PM INVITED PAPER

SYNTHESIS OF ZIRCONIA-8WT.% YTTRIA NANOCOMPOSITE BY PLASMA SPRAY: *Ramasis Goswami*[1]; Guo-Xiang Wang[1]; Sanjay Sampath[1]; Herbert Herman[1]; [1]SUNY at Stony Brook, Dept. of Mats. Sci., Stony Brook, NY 11794-2275 USA

Zirconia-8wt.% Yttria has been plasma sprayed to a thickness of 2mm on a steel substrate kept at two different temperatures. A fine dispersion of monoclinic phase with a size range of 5-20nm has been observed to be embedded at the cell boundary of metastable tetragonal (t') phase when it is deposited on a steel substrate held at 100ϒC. At a higher substrate temperature (450ϒC) an alternate layer of thick metastable tetragonal and very thin monoclinic phases was observed. The microstructural transition observed in this experiment has been explained by the use solute trapping models.

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DYNAMIC CALCULATIONS FOR PARTICLE PUSHING: *Carlos Enrique Schvezov*[1]; [1]University of Misiones, Faculty of Sciences, 1552 Azara St., Posadas, Misiones 3300 Argentina

The interaction of particles with a solidifying interface is studied dynamically employing mathematical modeling. The two main physical forces involved which are the drag and pushing force, are calculated for different particle and interface morphologies. Both forces are integrated analytically and the dynamic equation resulting from application of Newton's law is integrated numerically. The pushing forces come from the Lifshitz-Van der Waals interactions. The results show stable steady state interactions for flat interface and spherical or flat particles. However for curved interface shapes the steady state is reached for values of the interface velocity and particle radius which depend on the curvature of the interface. In the present report the results of the calculations are presented and the conditions for pushing are discussed.

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HETEROGENEOUS NUCLEATION ON CATALYTIC PARTICLES: *P. G. Höckel*[1]; G. Wilde[1]; J. H. Perpezko[1]; [1]University of Wisconsin-Madison, Dept. of Mats. Sci. and Eng., 1500 Eng. Dr., Madison, WI 53706 USA

Crystallization studies on undercooled droplets and bulk samples offer an effective method to examine nucleation kinetics due to catalysis by primary phases and incorporated particles. Droplet studies, where the interface between primary solid and the undercooled liquid acts as the catalytic substrate for heterogeneous nucleation, can provide information on nucleation behavior which is crucial for solidification modeling. In order to identify nucleation mechanisms, controlled thermal cycles have been performed in eutectic and peritectic systems. The results suggest some deficiencies in the spherical cap model of catalysis and identify new directions for kinetics analysis and modeling. Experiments on bulk samples of Cu and Ni containing inoculant particles yielded various amounts of undercooling, exceeding 200K for some composite systems following fluxing with a glass slag. The results indicate that many crystalline particles can be relatively inert in nucleation catalysis. The support of NSF (DMR-9712523) and NASA (NAG8-1278) is gratefully acknowledged.

5:15 PM INVITED PAPER

DIRECT NUMERICAL SIMULATION OF DENDRITIC MICROSTRUCTURES: *N. Provatas*[1]; N. Goldenfield[1]; *J. A. Dantzig*[1]; [1]University of Illinois at Urbana-Champaign, Dept. of Mech. and Indust. Eng., Dept. of Phys., Urbana-Champaign, IL 61801 USA

Prof.Glicksman has made invaluable contributions to the understanding of pattern selection during dendritic solidification. His experiments have served to guide the theoretical development of the industrially important problem. In this talk, we describe recent computations using phase-field models to directly simulate dendritic growth. In this method, the liquid-solid interface is modeled as a diffuse region whose thickness is characterized by an order parameter, known as the phase field. One of the difficulties encountered when applying the phase field method is the conflicting requirements of high resolution needed to successfully capture the physical phenomena at the interface, and the simultaneous need to fully resolve the diffusion field ahead of the advancing front. We employ an adaptive gridding procedure for solving the phase field equations, where high resolution is available near the interface, and more appropriate grid dimensions are used to resolve the diffusion field. Examples are given comparing calculations to experimental results from Prof. Glicksman's experiments.