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

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

Wednesday AM Room: 15B
March 3, 1999 Location: Convention Center

Session Chair: Reginald W. Smith, Queen's University, Dept. of Mats. and Metall. Eng., Kingston K7L 3N Canada

8:30 AM

TEMPUS CONTAINERLESS PROCESSING FACILITY FOR SPACE STATION - PRELIMINARY DESIGN AND SPECIFICATION: *J. Piller*[1]; A. Siedel[1]; M. Stauber[1]; W. Dreier[2]; [1]Dornier Gambh, Daimler-Benz Aerospace, Friedrichshafen D-88039 Germany; [2]Deutsches Zentrum fur Luft-und Raumfahrt (DLR), Bonn D-53227 Germany

The containerless processing facility TEMPUS was successfully used for electromagnetic levitation experiments during the MSL-1 Spacelab mission in 1997. Scientific goals have been the study of nucleation statistics and solidification speeds in undercooled melts, and the determination of thermophysical properties of the melt above and below the melting point. For future research in this promising field the accommodation of an Advanced TEMPUS facility on board of the International Space Station is under discussion. The results of a design study are presented to show that the well-proven technology of TEMPUS Spacelab can be transferred to a Space Station facility. In particular to better serve the individual and often interfering experiment requirements exchangeable experiment containers shall be made available for processing which are equipped with a set of samples, coil system, windows and other experiment specific devices.

8:50 AM

SCIENCE OPPORTUNITIES OF THE MATERIALS SCIENCE LABORATORY (MSL): *A. Lundstrom*[1]; P. Behrmann[1]; H. Lenski[2]; C. Cordelle[3]; [1]ESA/ESTEC, P.O. Box 299, AG, Noordwijk NL-2200 The Netherlands; [2]DASA-Dornier, Friedrichshafen Germany; [3]SNECMA-SEP, Villaroch France

The European contribution to the microgravity payloads of International Space Station includes the Materials Science Laboratory (MSL), which is part of ESA Microgravity Facilities for Columbus programme. MSL is a multi-user facility intended to support four areas of microgravity research: solidification physics, Bridgeman crystal growth crystal growth by zone processing and measurement of thermo physical properties. MSL will be developed in two versions: one to be accommodated in NASA's Materials Science Research Facility in the US-module and one self-standing facility for Columbus. The MSL provides a unique scientific flexibility by its concept of exchangeable furnace inserts and will by this concept support different branches of high temperature research. So the Low Gradient Furnace (LGF) insert is optimised for crystal growth of semiconductors and electronic materials under restricted, well-controlled thermal gradients. The Solidification and Quenching Furnace (SQF) is mainly intended for metallurgical solidification under strong gradients with the possibility of quenching the solidification interface at the end of processing. The furnace insert concept also supports incorporation of furnaces from international partners or external customers into MSL; NASA's Quench Module Insert (QMI) and Diffusion Module Insert (DMI) as well as the German Float-zone furnace with Magnetic Field (FMF) are presently in the planning. For the experiment cartridge, various diagnostics and stimuli are offered, including high-resolution thermocouples, Peltier pulsing, shear cell activation for diffusion experiments and reservoir heating. The scientific performance of MSL is further enhanced by the concept of experiment-dedicated electronics, which allows incorporation diagnostics targeted to individual experiments. In this context ESA is studying Seebeck voltage and resistance measurement and ultrasonic measurement of the solidification velocity, but this interface will also allow for e g video observation or PI-developed electronics.

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THE EUROPEAN FLUID SCIENCE LABORATORY (FSL) A HIGHLY FLEXIBLE, MODULAR MULTI-USER FACILITY: *J. R. Becker*[1]; H. Mundorf[1]; Cestmir Barta[1]; [1]ESA/ESTEC, TOS-MMG, P.O. Box 299, AG, Noordwijk NL-2200 The Netherlands

The FSL is one of the large multi-user facilities being developed under ESA's Microgravity Facilities for Columbus (MFC) Programme. Extending ESA's earlier fluid science research programs, the FSL will allow, among others, for the investigation of areas such as flows and induced instabilities, diffusive instabilities, interfacial tension and adsorbtion mechanisms, mechanisms of boiling, critical point phenomena, crystal growth and directional solidification within transparent media. Owing to its adaptable diagnostic tools and its modularity on several levels, complementary science areas such as colloid and aerosol physics, particle agglomeration and plasma crystal physics are envisaged. FSL's most important diagnostic tools are four different types of interferometers. An electronic speckle pattern interferometer (ESPI), a differential (shearing) interferometer and a holographic interferometer for measurements on transparent media and in addition an ESPI to perform surface measurements. For the first time in the history of microgravity facilities these diagnostics tools will become available on one facility by converting one type of interferometer into another by switching of optical components. Each type of interferometer represents unique features in terms of spatial resolution, time resolution and dynamic range in such a way, that the scientist will be able to select the best choice with respect to his particular experiment. Compared with earlier facilities, such as the Bubble, Drop and Particle Unit (BDPU), flown on Spacelab, FSL offers a greatly enhanced flexibility by having a larger exchangable experimental volume (the 'Experiment Container (EC)'), intelligent interfaces and modularity down to that level, improved control capabilities and extended research autonomy. The large experimental volume together with the intelligent interfaces will even allow for the application of dedicated three-dimensional measurement tools. The introduction of electronic imaging improves the telescience performance significantly.

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CSK-1C, TITUS AND ADVANCED TITUS FACILITIES FOR MATERIALS EXPERIMENTS IN SPACE: *Cestmir Barta*[1]; [1]BBT-Materials Processing, Doubicka 11, Prague 8, Czech Republic 184 00 Russia

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-Materials 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 now 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 metallurgical 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.

9:50 AM BREAK

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QUALITATIVE AND STATISTICAL ANALYSIS OF CELLULAR ARRAYS IN DIRECTIONAL SOLIDIFIED SUCCIONITRILE-ACETONE: *B. Kauerauf*[1]; G. Zimmermann[1]; S. Rex[1]; [1]Access e.V., Intzestr. 5, Aachen 52072 Germany

Two-dimensional cellular arrays which occurred during directional solidification in a Bridgman configuration under microgravity conditions in the transparent alloy succinonitrile-acetone were evaluated with respect to the time dependent behaviour of the pattern. Images of the cellular patterns observed in-situ in top view from the melt by an endoscope optic show continuous restructuring of the cellular patterns accompanied by arising and elimination of cells on a time-scale of several minutes. Contrary to this qualitative analysis a statistical quantitative evaluation of pattern characteristics shows no significant changes in the primary spacing of the cells or in the distribution of the cell sizes. Therefore, it can be concluded that during the directional solidification a steady-state for the patterns was reached without changes in quantitative characteristics but with a continuous rearrangement of the structure.

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NUMERICAL SIMULATION OF MONOTECTIC SOLIDIFICATION USING PHASE-FIELD MODEL: *Y. Arikawa*[1]; J. B. Andrews[1]; S. R. Coriell[2]; W. F. Mitchell[2]; [1]University of Alabama at Birmingham, Dept. of Mats. and Mech. Eng., Birmingham, AL 35294 USA; [2]National Institute of Standards and Technology, Gaithersburg, MD USA

A numerical simulation scheme using a phase-field formulation has been constructed to model a directional solidification front in monotectic systems. The scheme has been tailored to suit the atypical characteristics of the underlying physical system, i.e. one of the product phases in the monotectic system is still liquid after the reaction. This atypical characteristics suggest a strong asymmetry in the production of latent heat at the interface which should have a impact on the microscopic interface curvature. Although the liquid-liquid interface and accompanying Marangoni flow at the interface are expected to play a role in determining the interface shape, inclusion of the effect of fluid motion into the model is still underway. Numerical results are compared to experimental results obtained for succinonitrile-glycerol system.

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LSW, LSEM AND MEAN FIELD THEORY DISTRIBUTIONS FOR Fe-Cu LPS MICROGRAVITY RESULTS: *J. Naser*[1]; Y. He[1]; S. Ye[1]; A. K. Kuruvilla[2]; J. E. Smith[1]; [1]University of Alabama in Huntsville, Consortium for Materials Development in Space and Dept. of Chemical & Materials Engineering, Huntsville, AL 35899 USA; [2]Marshall Space Flight Center, IITRI/MRF, Bldg. 4618, MSFC, AL 35812 USA

Testing coarsening theories against experimental LPS results is complicated by the gravity driven convection in unit gravity. The absence of gravitational force in microgravity represents a unique environment for testing coarsening theories. Lifshitz Slyozov and Wagner theory (LSW) and the modified Lifshitz Slyozov Encounter Modified theory (LSEM) distributions were compared against experimental results obtained from microgravity processed liquid phase sintered Fe-Cu samples. The agreement between the LSEM and the experimentally measured distributions were far better than using LSW theory. The mean Field theory did not fit the experimental distribution as well as the LSEM, but predicted a better cut off than the LSW distribution. The reason for this disparity resulted from the fact that Fe-Cu had agglomerated particles and copper pools. Results for several systems, and proposed theory modification will be presented.

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THE THERMOPHYSICAL PROPERTIES OF Zr-Nb-Ni-Cu-Al AND Zr-Ti-Ni-Cu GLASS FORMING ALLOYS: *Charles G. Hays*[1]; Jan Schroers; William L. Johnson[1]; [1]California Institute of Technology, Dept. of Mat. Sci. 138-78, Pasadena, CA 91125 USA

The thermophysical properties of the recently discovered bulk metallic glasses are an area of both scientific and technological interest. To further our understanding of the glass forming ability of these alloys a ground-based examination of the undercooling behavior in these alloy systems was implemented using the Electrostatic Levitation (ESL) technique. This paper presents results of undercooling and step modulation calorimetry measurements conducted on two bulk glass forming alloy systems: Zr-Nb-Ni-Cu-Al and Zr-Ti-Ni-Cu. In each system large undercooling levels of the order of 225K were observed. The undercooling was found to be dependent on the degree of overheating above the liquidus temperature. Discontinuous levels of undercooling were observed for overheats of 300K. The properties of the ESL processed specimens were examined by x-ray diffraction, electron- and optical-microscopy, and thermal analysis. The ESL results are compared with the results from the MSL-1 space shuttle flight experiments. The experimental results are discussed in relation to the predictions of classical nucleation theory and are related to the known features of the multicomponent phase diagrams.

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CHARACTERIZATION OF A CERAMIC SPRING FOR USE IN SEMICONDUCTOR CRYSTAL GROWTH IN MICROGRAVITY: *Monica L. Kaforey*[1]; Christopher W. Deeb[1]; David H. Matthiesen[1]; [1]Case Western Reserve University, Dept. Mat. Sci. & Eng., 10900 Euclid Ave., White 330, Cleveland, OH 44106 USA

Traditionally, semiconductor crystals have been grown in microgravity to reduce convection in the hopes of achieving diffusion controlled growth. In many of these experiments, a ceramic spring was used to prevent free surface formation to avoid Marangoni convection. Pyrolytic boron nitride (PBN) leaf springs will withstand the temperature and atmosphere requirements for the growth of semiconductor materials such as germanium and gallium arsenide. A theoretical model based on a simply supported section cut from a cylinder was developed to predict the spring constant of a stack of PBN leaf springs. Experiments were done, based upon a statistically rigorous design of experiments (DOE), in which the spring constant was measured. The experimental data was empirically fit with a full quadratic model in terms of 4 variables: spring width, spring thickness, spring radius, and the number of springs in the stack. The empirically fit model was compared with the theoretically developed model.

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AN OVERVIEW OF THE ELECTROSTATIC LEVITATION FACILITY AT NASA'S MARSHALL SPACE FLIGHT CENTER: *Jan R. Rogers*[1]; Michael B. Robinson[1]; Larry Savage[1]; Wolfgang Soellner[1]; [1]NASA/MSFC, ES76, Marshall Space Flight Center, Huntsville, AL 35812 USA

Containerless processing represents an important area of research in microgravity materials science. This method provides access to the metastable state of an undercooled melt. Containerless processing provides a high-purity environment for the study of reactive, high-temperature materials. Reduced gravity affords several benefits for containerless processing, for example greatly reduced positioning forces are required and therefore samples of greater mass can be studied. Additionally in reduced gravity, larger specimens will maintain spherical shape which will facilitate modeling efforts. Space Systems/LORAL developed an Electrostatic Containerless Processing System (ESCAPES) as a materials science research tool for investigations of refractory solids and melts. ESCAPES is designed for the investigation of thermophysical properties, phase equilibria, metastable phase formation, undercooling and nucleation, time-temperature-transformation diagrams and other aspects of materials processing. These capabilities are critical to the research programs of several Principal Investigators supported by the Microgravity Materials Science Program of NASA. NASA's Marshall Space Flight Center (MSFC) recently acquired the ESCAPES system from LORAL. MSFC is now developing a levitation facility to provide a critical resource to the microgravity materials science re-

search community to continue and enhance ground-based research in the support of the development of flight experiments during the transition to Space Station.

ABATEMENT OF GREENHOUSE GAS EMISSIONS IN THE METALLURGICAL & MATERIALS PROCESS INDUSTRY

Sponsored by: Extraction & Processing Division, Waste Treatment & Minimization Committee

Program Organizers: C. Lupis, MIT, Room 13-5114, Cambridge, MA 02139 USA; V. I. Lakshmanan, Ortech Corporation, Mississauga, Ontario L5K1B3k Canada

Wednesday AM Room: 1B
March 3, 1999 Location: Convention Center

Session Chairs: Claude Lupis, MIT, Materials Science and Engineering, Cambridge, MA 02139 USA; V. I. Lakshmanan, Mississauga, Ontario L5K1B3k Canada

8:30 AM INTRODUCTION

8:40 AM
CO2 REDUCTION STRATEGIES IN THE BASIC METALS INDUSTRY: A SYSTEMS APPROACH: *Dolf J. Gielen*[1]; *Antonius W. N. VanDril*[1]; [1]ECN, Beleidsstudies, P.O. Box 1, Westerduinweg, Petten, Noord-Holland 1755 ZG Netherlands

To find strategies for reducing greenhouse gas emissions in the basic metals industry, a study is made for the Western European steel and aluminium market up to 2020. Taken into account are competition of cheap energy locations, alternative policy scenarios for CO2/energy taxes, energy efficiency improvement for existing technologies, new technologies for iron and steelmaking, additional CO2 removal technologies, possibilities and limitations for recycling, and improved materials efficiency in product manufacturing. These strategies are simultaneously analysed within a MARKAL model approach that includes the energy supply system. Results state that a factor two reduction of CO2 is readily attainable. Favourable solutions for steel include DRI combined with EAF and new Cyclone converter technology. CO2 removal and the CO2 emission for electricity generation are essential factors. The limitation for recycling is scrap availability, rather than quality. For aluminium, scrap availability and the electricity emission factor are essential limitations. However, taking all options into account, greenhouse gas reductions with a factor 5 to 10 are attainable for the European basic metals industry.

9:05 AM
CO2 EMISSIONS AND THE STEEL INDUSTRY'S POSSIBLE RESPONSES TO THE GREENHOUSE EFFECT: *Jean-Pierre Birat*[1]; Yann de Lassat[2]; Michel Schneider[2]; Michel Jeanneau[2]; [1]IRSID, BP 30320, Maizieres-les-Metz 57283 France; [2]Usinor, Cours Valmy, Paris-La-Defense France

The Steel Industry, is responsible in France for 6% of CO_2 emissions, through a small number of large sources. The carbon consumption of the Steel Industry ends up eventually as CO_2 in the atmosphere, to a level which is directly proportional to the amount of steel production. In 1989, the French Steel Industry used 423kg of carbon per ton of rolled steel, which means emissions of 1550kg of CO_2 per ton. Globally, for a 16.9Mt production, this adds up to 26.3Mt CO_2; the energy savings policy, which has been rigourously enforced since before the first energy crisis, has led in France to a reduction of carbon consumption from 1100kg/t of steel to 423kg/t over this period of 20 years. This result has been achieved thanks to radical modifications of process routes and to better process control: increase in the size of reactors such as the blast furnace or the basic oxygen converter, general introduction of strand sintering and continuous casting, increase in the number of electric furnace steelshops are typical examples of such changes; the carbon which the Steel Industry uses today is close to the minimum amount that is required by process thermodynamics and technologies. An exhaustive assessment of steel production processes, either existing, under development or still in the research field, has been carried out in terms of CO_2 emissions, using process models available at IRSID. Industrial realism has been introduced by taking into account the magnitude of available sources of iron, by estimating time for process development when a process route is not readily available in the industry, and by balancing various possible processes against the quality needs of the product mix that a modern steel production company has to make available to customers. The major conclusions are as follows: energy savings should be continued, especially in countries where the actions outlined before have not yet all been made (step 1); another step would consist in substituting iron ore by scrap, within the limits set by product quality and by the availability of recycled steel. This should be easier to carry out in developed countries, where scrap should become more readily available, due to used metal accumulation and to government regulations that foster materials recycling. Typically, scrap use could go up from 35 to more than 50% of source iron in a country like France (step 2); beyond that, other solutions are possible, although they are not cost effective today. The use of plasma torches in the blast furnace on a year round operation and also natural gas or hydrogen prereduction are typical examples (step 3).

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THE ABATEMENT OF CO2-EMISSIONS IN THE PRODUCTION OF FERROALLOYS: *Tor Lindstad*[1]; [1]SINTEF, Materials Technology, Alfred Getz vei 2B, Trondheim N-7034 Norway

Specific CO2-emissions are given for the production of silicon-metal, ferrosilicon, silicomanganese, ferromanganese and ferrochrome. Emissions come from the mining of raw materials and reduction materials, from coke production and generation of electric energy. CO2-emissions can be abated by direct and by indirect methods. A direct method is to replace fossil carbon as reduction material wholly or partially by endogenous carbon (biocarbon, charcoal). Another possibility is to produce metals by electrolysis instead of the present electric smelting furnace. Indirectly CO2-emissions can be reduced by energy recovery in the off-gas, thus saving coal, oil or natural gas for heat generation. Some reduction of global CO2-emissions can be obtained by giving credit for the use of silica dust partially replacing cement in concrete. In addition to an overview of possible methods, costs will be discussed.

9:55 AM
ABATEMENT OF SOX EMISSIONS IN RELATION WITH BASIC METAL SULFIDES PROCESSING: *Ibrahim Gaballah*[1]; Eric Allain[2]; Ndue Kanari[1]; Kawan Malau[3]; [1]INPL - CNRS, ENSG-LEM, 2 Avenue de la foret de Haye, BP 3, Rue du Doyen M. Roubault, BP 40, Vanduvre F - 54501 France; [2]University of Missouri Rolla, Dept. of Metall. Eng., 215, Fulton Hall, Rolla, MO 654098 USA; [3]Mineral Technology Development Center, Jalan Jenderal Sudiman 623, Bandung Indonesia

About forty percent of the SOx emissions are generated during the processing of metal sulfides of Cu, Pb, Zn, Ni, etc. Although new technologies for metal sulfide's smelting allow the production of H2SO4 with a reasonable cost and decrease the emissions of sulfur oxides, the generated quantity of SOx is considered as a serious threat to environment. This paper suggests alternatives for low temperature processing of complex sulfide concentrates "CSC" under neutral, reducing and chlorinating atmospheres or their combination. The neutral and reducing treatments, at T > 400ϒC, allow the decomposition of pyrite and the partial recovery of sulfur as Sϒ; and H2S. At 300ϒC, the chlorinating treatment of CSO is fast, exothermic and allows the separation of FeCl3 from the valuable elements: chlorides. It also generates SyClx that can be either reduced by H2 or hydrolyzed in presence of sodium sulfide. The recovery rate of elemental sulfur with respect to the sulfur input exceeds 90 percent.

10:20 AM BREAK

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MORE PROGRESS IN IMPLEMENTING THE ALUMINUM TECHNOLOGY ROADMAP: *Jack Eisenhauer*[1]; *Henry Kenchington*[2]; John Green[3]; [1]Energetics, Inc., 7164 Gateway Dr., Columbia, MD 21046 USA; [2]U.S. Department of Energy, Office of Industrial Technologies, 1000 Independence Ave., Washington, D.C. 20585 USA; [3]The Aluminum Association, 900 19th St., Washington, D.C. 20006 USA

Leaders in the U.S. aluminum industry have recognized that success in the competitive global marketplace will depend on new business strategies that leverage R&D investments across industry and government. To this end, the aluminum industry has entered into a partnership with the U.S. Department of Energy's (DOE's) Office of Industrial Technologies (OIT) to address issues of competitiveness, the environment, and energy use from a long-term perspective. The Aluminum Industry Technology Roadmap published in 1997 has laid out concrete technology strategies for achieving industry goals and has established a focused research and development agenda for aluminum. A follow-on technology roadmap on inert anodes addresses one of the highest priorities in the first roadmap, the development of inert (non-consumable) anodes that can reduce emissions of CO_2 and perfluorocarbons from smelting. A separate technology roadmap focusing on R&D that will facilitate the use of aluminum in the automotive market is currently being developed. This effort complements technology roadmap activities undertaken by the U.S. automotive industry as part of the Partnership for a New Generation of Vehicles. As a result of the aluminum industry's roadmapping efforts, a number of collaborative R&D projects have been launched and are making considerable progress.

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PRIMARY ALUMINUM PRODUCTION: PROJECTED GREENHOUSE GAS EMISSIONS AND THE COSTS OF CLIMATE CHANGE POLICY: *Jochen Harnisch*[1]; Ian S. Wing[1]; Ron G. Prinn[1]; Henry D. Jacoby[1]; [1]Massachusetts Institute of Technology, Joint Program on the Science and Policy of Global Change, 77 Massachusetts Ave., Building E40-390, Cambridge, MA 02139-4307 USA

Climate policy may gain significant influence on investment decisions made associated with the production of primary aluminum. This work is intended to demonstrate the potential of an integrated analysis for an improved understanding of the environmental effectiveness and economic consequences of different climate policies. In this study we first compare atmospheric observations to the available emission estimates for CF_4 and C_2F_6 for the baseline years 1990 and 1995. We then present projections for regional emissions of PFCs from the aluminum industry under different climate change policy scenarios using the MIT Emission Projection and Policy Analysis (EPPA) energy-economy model. Finally, we use CO_2 abatement costs to analyze the environmental effectiveness of investments into emission reductions of PFCs in the context of the Kyoto-protocol.

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A BIOMIMETIC APPROACH TO CO2 REMEDIATION: *Gillian M. Bond*[1]; Gerald Egeland[1]; Donald K. Brandvold[2]; Margaret Gail Medina[1]; John Stringer[3]; [1]New Mexico Tech, Materials & Metallurgical Engineering, Campus Station, Socorro, NM 87801 USA; [2]New Mexico Tech, Chemistry, Campus Station, Socorro, NM 87801 USA; [3]Electric Power Research Institute, 3412 Hillview Ave., Palo Alto, CA 94304 USA

Public concerns over the "greenhouse effect" have resulted in research efforts into various possible approaches to CO_2 remediation. Fixation of CO_2 into calcium carbonate is potentially an ideal way of disposing of the large quantities of CO_2 produced by many industrial processes. It is a proven method in geological terms, with an environmentally friendly end product. Early in the earth's geological history, the atmosphere contained around three orders of magnitude more CO_2 than it does now. This level gradually decreased as large quantities of carbon became locked up in various reservoirs, of which carbonate minerals, notably limestone and chalk, comprise a major example. Much of the deposition into carbonate reservoirs occurred biologically, through the action of a variety of marine organisms. The problem with such an approach to commercial CO_2 remediation, of course, is one of rate. We have followed a biomimetic approach to accelerating CO_2 sequestration; we have examined the chemistry of CO_2 fixation into calcium carbonate in aqueous solution, and the rate-limiting steps, and then considered what lessons we could learn from biological systems in terms of how to accelerate those steps. As a result, we are studying an enzymatic approach to accelerated CO_2 sequestration, in which carbonic anhydrase is used to catalyze the hydration of CO_2.

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HIGH-TEMPERATURE SOLAR THERMOCHEMISTRY FOR GREENHOUSE GAS MITIGATION IN THE EXTRACTIVE METALLURGICAL INDUSTRY: *Jean P. Murray*[1]; Aldo Steinfeld[2]; [1]Colorado School of Mines, Engineering, Golden, CO 80401 USA; [2]Paul Scherrer Institute, Solar Process Technology, Villigen PSI 5232 Switzerland

The extractive metallurgical industry is a major consumer of high-temperature process heat. It is, consequently, a major contributor of CO2 emissions and other greenhouse gases derived from the combustion of fossil fuels for heat and electricity generation. These emissions can be substantially reduced by replacing fossil fuels with solar energy as the source of process heat. Concentrated solar radiation can supply thermal energy to endothermic reactions at temperatures exceeding 2000 K. Examples of metal oxides reduction processes that have been studied experimentally in solar furnaces include the production of Fe, Al, Mg, Zn, TiC, SiC, CaC2, TiN, Si3N4, and AlN by carbothermic reduction of their oxides in Ar or N2 atmospheres.

ALUMINA AND BAUXITE: Bayer Process Design and Simulation

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

Wednesday AM Room: 6E
March 3, 1999 Location: Convention Center

Session Chair: Seymour Brown, Kaiser Aluminum & Chemical Corporation, Gramercy Works, Gramercy, LA 70052 USA

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SIMULATIONS OF BAYER LIQUOR PIPEFLOWS USING A ROTATING CYLINDER ELECTRODE: *N. Andy Darby*[1]; Chris J. Newton[1]; Jonathan D. B. Sharman[1]; [1]Alcan International, Ltd., Banbury Laboratory, Southam Rd., Banbury, Oxon OX16 7SP England

The investigations of flow-related corrosion and erosion occurring in process plants can be aided by the use of a rotating cylinder electrode. Effects of changes in flow velocity, liquid composition and operating temperature can be considered using a relatively small scale apparatus. To achieve successful simulations of plant conditions, a reliable method of correlating plant flows with those present in this type of laboratory equipment is necessary. It is necessary to include thermophysical fluid property data since many plants, such as those in the alumina industry, operate at temperatures and pressures significantly above ambient. Also, Bayer process plants operate with finely divided solids slurries and turbulent flow regimes are utilised to ensure particulates are transported in suspension to prevent scaling of pipework. This paper extends the theories put forward by Silverman and allows a much wider range of fluid Reynolds numbers to be used as well as the characterisation of a rotating drum/cylinder device in use for errosion/corrosion testing at Alcan.

9:00 AM

SIMULATION OF THE BAYER PROCESS: *Emmanouil C. Papadopoulos*[1]; Olga Dimitropoulou[1]; Ioannis L. Paspaliaris[1]; [1]National Technical University of Athens, Laboratory of Metallurgy, Zografou Campus, Zografos, Athens GR 157 80 Greece

Today, off-the-shelf personal computers have enough power to perform complicated calculations of material and energy balance in an extremely short time. In order to study the response of the Bayer Process to various changes in its parameters, a simulation tool was developed in the Laboratory of Metallurgy. The tool was developed

using an object oriented programming language (Microsoft VC++) and can be run under any MS-Windows 32 bit operating system. The simulation tool was developed so that it could be easily operated by anyone with a minimum working knowledge of Windows and that no programming experience should be required. The result of this effort is a complete graphical user interface, which is easy to use and yet gives the flexibility to explore the different possibilities in the flowsheet design. Because of the modular approach, the same tool can be applied to simulate other steady state hydrometalurgical processes. An example is presented showing the close agreement of the model with those from an existing alumina plant.

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1998 VISIONS OF THE FUTURE BAYER PROCESS: *Lester A. D. Chin*[1]; [1]Chin's Consultants International, Inc., 426 Kibbee Rd., McDonough, GA 30252 USA

Karl Joseph Bayer invented and patented the Bayer Process in 1888, and in 110 years since its invention, Bayer Technologists have modified and developed the Process to economically supply the growing aluminium and alumina chemicals industries with Smelter-Grade Alumina and alumina chemicals feedstocks of the desired qualities from different bauxites, under increasing costs of fuels and energy, under increasing concerns for the environmental impacts of the industries and in the environments of developing countries where some bauxites are found. A Bayer Technologist's visions of the future Bayer Process are presented, with the suggestion that some of these visions must be developed to continue the provision of viable solutions to the future challenges of our industries, posed by (a) decreasing grades of bauxite, (b) more stringent Product quality requirements, (c) more stringent environmental requirements for bauxite mining and alumina refining operations, and (d) increasing costs of operating supplies such as fuels, energy, and caustic soda.

10:00 AM BREAK

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ENERGY UTILISATION AND COST REDUCTION IN ALUMINA REFINERIES: *John McFeaters*[1]; [1]Queensland Alumina, Ltd., Parsons Point, Gladstone, Queensland 4680 Australia

Energy comprises a significant proportion of the cost of alumina refining and consequently offers a large potential for cost reduction. Pinch technology can be used to help analyze energy use and identify potential areas for savings. Although, in general, larger opportunities are often limited by process, capital or logistical constraints. However, there are often good opportunities for energy savings through operational and maintenance practices and strategies. These opportunities usually result in less capital intensive projects which do not significantly affect the process. This paper includes a generalized analysis of energy utilization in high temperature alumina plants and the development of guidelines for evaluating energy utilization, identification of potential savings and continuous monitoring of energy efficiency. The paper focuses on energy cost reduction through operation and maintenance practices and control strategies.

11:00 AM
CO-GENERATION—AN EFFECTIVE AND ECONOMIC SOLUTION TO POWER INSTABILITY: *B. K. Mishra*[1]; R. Waris[1]; [1]National Aluminium Company, Ltd., Mines and Refinery Complex, Damanjodi District, Koraput, Orissa 763008 India

Uninterrupted power supply to an alumina refinery assumes great importance for its continuous operation as well as to keep many of its vital equipment in healthy state, even when they are not engaged for achieving production. In various units of the Bayer circuit, bauxite, mud or hydrate slurry, with solid consistency varying between 10-50%, power interruptions for a prolonged period can cause major damage to equipment resulting in production and financial losses. Therefore, it becomes obligatory for alumina plants to have an uninterrupted power source especially when a state owned grid is unstable because of a wide gap between supply and demand. Co-generation of power which generates both electricity and process steam is an effective and economic means to solve the problems associated with power supply instability. The paper highlights the benefits associated with establishing a co-generation unit and its economics at the 800,000 MTPY, NALCO, alumina refinery in Orissa, India.

ALUMINUM ALLOYS FOR PACKAGING IV: Session I — General

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

Wednesday AM Room: 3
March 3, 1999 Location: Convention Center

Session Chair: Subodh K Das, ARCO Aluminum Inc., Louisville, KY 40232 USA

8:30 AM INVITED PAPER
WILL PET DO TO ALUMINUM CANS WHAT ALUMINUM DID TO STEEL?: *Firoze Katrak*[1]; [1]Charles River Associates, Inc., 200 Clarendon St., T-33, Boston, MA 02116 USA

Aluminum containers have lost a significant share of the market to PET over the last few years. What are the key issues driving the competition among aluminum, PET, and steel for soft drink and other types of containers? How do they differ globally? Also, given the different rates of growth for soft drink containers around the world, what are the overall implications for aluminum? This paper will discuss key issues related to the future use of aluminum in containers.

9:00 AM INVITED PAPER
ALUMINUM BEVERAGE CAN STOCK- ENTERING THE 21ST CENTURY: *Tom Thomsen*[1]; [1]231352 Loges Lane, Evergreen, CO 80439 USA

This presentation will include-growth of the beverage industry, global consolidation, threat of plastic & glass bottle, global can makers, can stock producers, and environmental issues.

9:30 AM
ALUMINUM PROPERTIES IN BEVERAGE CANS DURING NECKING: *Dean Johnson*[1]; [1]Ball Packaging Operations, Research Dept., 9343 W. 108th Ave., Broomfield, CO 80021 USA

It is safe to say that the beverage can industry finally understands how to neck 204 and 202 beverage cans at the current gauge. It is the industry challenge to reduce the metal in the can once again. The largest hurdle seems to be reducing the metal in the neck area. In order to understand the necking operation, we need to investigate the metal properties during the entire can making process. There have been several good papers written on necking and how the metal properties change through the necking operations. This paper will further investigate how the metal properties change in the Die Necking process and Spin Necking process.

10:00 AM INVITED PAPER
OPPORTUNITIES, PROBLEMS, AND PERILS FOR ALUMINUM IN PACKAGING: *George J. Binczewski*[1]; [1]SC Systems, P.O. Box 6154, Moraga, CA 94570 USA

The enormous tonnage of aluminum consumed for packaging usages raises serious concerns when semblances of a decline in various sectors are intimated or actually experienced. Significant changes occurring in the associated aluminum manufacturing operations have raised profound questions about the future. Some of the reasons for this are openly obvious while others are somewhat subtle, seldom mentioned and should be examined. Various aspects of the most relevant factors involving fabrications, applications, marketing, and recycling are discussed and recommendations for achieving positive results are made.

ALUMINUM REDUCTION TECHNOLOGY: Prediction & Validation of Performance

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

Wednesday AM Room: 6F
March 3, 1999 Location: Convention Center

Session Chair: John Chen, The University of Auckland, Dept. of Chem. & Mats. Eng., Auckland 1001 New Zealand

8:30 AM
WHY 'BEST' POTS OPERATE BETWEEN 955 AND 970ϒC: *T. A. Utigard*[1]; [1]University of Toronto, Metallurgy & Mat. Science, 184 College St., Toronto, Ontario M5S 3E4 Canada

From fundamental physical and chemical properties of the electrolyte it is shown that for the Hall- Heroult process, the optimum operating temperature is in the range from 955 to 970ϒC. This corresponds to an electrolyte containing 9 to 12 wt% excess AlF_3, 4 to 7 wt% CaF_2 and 2 to 4 wt% Al_2O_3. For operations using LiF, the optimum operating temperature can be lowered by approximately 10ϒC. The present analysis which is supported by industrial practice, is based on i) phase diagrams, ii) density behavior, iii) aluminum-electrolyte interfacial tension, iv) electrolyte electrical conductivity, and v) heat loss through sidewalls and cathode bottom.

9:05 AM
INSTABILITY MECHANISMS IN ALUMINIUM REDUCTION CELLS: *P. A. Davidson*[1]; W. R. Graham[1]; H. O'Brien[1]; [1]Univeristy of Cambridge, Dept. of Engineering, Trumpington St., Cambridge CB2 1PZ UK

We have developed a simple model of reduction cell instabilities which highlights the critical role played by the cryolite thickness. We have extended the model to incorporate movement of the anode blocks and have investigated the effect of small, controlled movements of these blocks. Using a simple control strategy we find that the stability threshold of a cell can, in principle, be greatly improved.

9:35 AM
EIGENMODES AND INTERFACE DESCRIPTION IN A HALL-HEROULT: J. P. Antille[2]; *J. Descloux*[1]; M. Flueck[1]; M. V. Romerio[1]; [1]Swiss Federal Institut of Technology, Dept. of Mathematics, Lausanne 1015 Switzerland; [2]Alusuisse Technology & Management, Ltd., Technology Center Chippis CH - 3965 Switzerland

In a series of papers, the authors have introduced a general method for calculating the stability of a Hall-Heroult cell with high accuracy. The stability of the fluid motions, and particularly the geometry of the interface between aluminum and bath, is modeled using a linearization of the magnetohydrodynamic equations around a steady-state solution of the full set of equations under the given operating conditions of the cell. Measurements were performed on an unstable cell, in which the current in the 16 anodes rods were recorded simultaneously. These measured currents are used as input disturbances to the stability model. The resulting slightly modified force field in turn excites the different modes of oscillation of the cell with amplitudes which are directly related to the amplitudes of the fluctuation of the current. The amplitudes of the different modes are thus determined, so that the time-dependent behavior of the different fields, in particular those of metal surface contour and of the velocity, can be described. A video-recording of the simulated metal surface will be presented.

10:00 AM
DIMENSIONING OF COOLING FINS FOR HIGH-AMPERAGE REDUCTION CELLS: *I. Eick*[1]; D. Vogelsang[1]; [1]VAW Aluminium-Technologie GmbH, Process Modelling, Georg-von-Boeselager-Str. 25, 53117 Bonn Germany

The heat generated in the bath region of high-amperage reduction cells has to be dissipated in a controlled manner to establish a stable side ledge which protects the potlining sufficiently. This can be achieved by designing the potlining of the cells using thermo-electric simulations which also take into account the cooling effect of the shell cradles. In cases of spatial restrictions, due to short distances inside the pot, strong metal flow against the ledge or insufficient ventilation between the pot shells, additional cooling fins welded to the pot shell can be used to avoid "hot spots" and vanishing side ledge thickness. The position and dimensions of such cooling fins can be designed using Computational Fluid Dynamics (CFD) simulations of the heat transfer conditions, assuming turbulent natural convection of the ambient air. The local heat transfer coefficients determined in this way can be implemented in thermo-electric heat balance models, thus offering the possibility to optimize the dimensions of the cooling fins and to analyze the impact of different ventilation conditions. Examples of computational results for different fin configurations are given. The calculated temperature fields and heat fluxes are compared to corresponding plant measurements.

10:25 AM BREAK

10:45 AM
DYNAMIC LEDGE RESPONSE IN HALL-HEROULT CELLS: *K. A. Rye*[1]; T. Eidet[2]; K. Torklep[2]; [1]Elkem Aluminium, R&D-Group, PB 566, Mosjoen N-8650 Norway; [2]Elkem Research, Aluminium Reduction, PB 40, Kristiansand N-4602 Norway

Measurements of the side ledge thickness, bath temperature, electrolyte composition and cell resistance have been performed to verify the dynamic response of Hall-Heroult cells to the extra heat generated during anode effects. Results indicate that melting of the freeze ledge is less severe than predicted by thermal models.

11:10 AM
THREE DIMENSIONAL MODEL FOR CURRENT EFFICIENCY BASED ON THE RATE OF ALUMINIUM TRANSFER TO ANODE: *M. F. El-demerdash*[1]; S. M. El-Raghy[1]; F. A. Moustafa[2]; [1]Cairo University, Faculty of Engineering, Cairo Egypt; [2]The Aluminium Company of Egypt, Cairo

The already published two dimensional model is developed to three dimensional model to estimate current efficiency of the Aluminium Cell. The transfer rate of a aluminium from cathode to anode is estimated as a result of diffusion and mass transfer under velocity field. The mixing differential equation in the homogenous conditions is solved numerically with suitable boundary conditions at Al / electrolyte and electrolyte / anode interfaces. The diffusion coefficient of aluminium in the electrolyte is taken as 1*10-8 m^2s and the maximum solubility of aluminium in electrolyte as 0.03 wt./wt. Results show the effect of three dimensional velocity field on current efficiency.

11:35 AM
SIDE LINING EFFECTS ON THERMAL BEHAVIOUR OF PREBAKED ALUMINIUM CELL: *S. M. El-Raghy*[1]; H. A. Ahmed[1]; S. A. Kaseb[1]; Z. Bassuony[2]; M. M. Ali[1]; [1]Cairo University, Metallurgical Engineering, Faculty of Engineering, Cairo Egypt; [2]Aluminium Company of Egypt, Cairo Egypt

A 203 KA prebaked cell has been designed and operated by Aluminium Company of Egypt (Egyptalum). The cells are side lined by carbon blocks of 20 cm thick at the top of the cell and 40 cm thick at the cathode bottom. One of the cells is side lined by 10 cm thick blocks of silicon carbide. The thermal behaviour of the cell which effects cell life and energy efficiency was determined using a computer thermal model. This model calculates bath temperature and temperatures across the side walls and the bottom of the cell, ledge profile and energy losses through different parts of the cell. The model was used to perform parametric studies to determine the effect of side lining material, namely, carbon and silicon carbide with different thicknesses on thermal behaviour of the cell. Theoretical analysis comparing the results with an actual cell is presented.

ANALYTICAL TECHNOLOGY IN THE MINERAL INDUSTRIES: Microbeam Techniques in the Mineral Industry

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

Wednesday AM Room: 7A
March 3, 1999 Location: Convention Center

Session Chairs: Steven L. Chryssoulis, Amtel, London, Ontario NG6 4X8 Canada; Stamen Dimov, Amtel, London, Ontario NG6 4X8 Canada

8:30 AM INTRODUCTORY REMARKS BY STEPHEN CHRYSSOULIS

8:40 AM INVITED PAPER
QUANTIFICATION OF SILICATE MINERALS BY SEM-BASED IMAGE ANALYSIS: *John Wilson*[1]; [1]Natural Resources Canada, CANMET/MMSL, 555 Booth St., Ottawa, Ontario K1A 0G1 Canada

An analytical program using a combination of SEM-based image analysis techniques is developed for automatic modal analysis of ores containing silicates and other gangue minerals. Previous knowledge of which minerals are present and their elemental composition is used to establish discrimination criteria in the image analysis program. The program initially discriminates minerals in polished section on the basis of relative grey values in a backscattered electron image. For those minerals which have overlapping grey levels the minerals are identified by energy dispersive X-ray spectrometry with X-ray counting of minerals grains for twelve or more elements. The minerals are quantified by measuring the accumulated areal proportion of each mineral over several fields. CANMET uses this technique to quantify gangue minerals where high accuracy is required. Two cases of application are presented.

9:00 AM INVITED PAPER
AUTOMATED PRECIOUS MINERAL SEARCH AND APPLICATIONS IN PROCESS MINERALOGY: *Rolando Lastra*[1]; Louis J. Cabri[1]; John M. D. Wilson[1]; [1]Natural Resources Canada, CANMET, 555 Booth St., Ottawa, Ontario K1A 0G1 Canada

An image analysis program, written at CANMET, performs an automatic precious minerals search. The program can search, for example, gold minerals in samples in polished sections. The search involves a meander of approximately 100x100 fields (BSE images) at a magnification of 400X. This magnification allows detection of gold grains as small as one micrometer in diameter. Typically, an overnight search of a -270+400 mesh product will scan ~300,000 particles, providing data not easily obtained by manual optical microscopy. The program consists of four parts: the location of grains of correct brightness, WDS dot mapping of such grains, filtering to remove artifacts and recording images and stage location for subsequent retrieval. At the end of the run, the program allows the operator to verify and identify grains classified as gold. CANMET has applied this gold search program in many studies of gold ores of commercial interest. Some case histories will be described.

9:20 AM
TIME-OF-FLIGHT RESONANT IONIZATION MASS SPECTROMETRY (TOF-RIMS) TRACE ELEMENT ANALYSIS OF PRECIOUS METALS IN MINERALS: *Stephen L. Chryssoulis*[1]; Stamen Dimov[1]; [1]AMTEL, 100 Collip Circle, UWO Research Park, London, Ontario N6G 4X8 Canada

Detection and quantification of precious metals (Au, Pd, Pt, and Rh) in rock minerals (quartz, silicates, and carbonates) is important for establishing the maximum attainable recovery. To achieve this goal subpart per billion (ppb) detection limits are required plus the ability to quantify results. Existing quantitative microbeam techniques (EPMA, PIXE, SIMS) have limits of detection in the 0.5-200ppm range. Time-of-flight resonant ionization mass spectrometry (TOF-RIMS) is a microbeam analytical technique that allows for the identification and quantification of atomic species in very small quantities. It utilized a tunable laser source for resonant excitation and ionization of a particular element of interest and has some unique features: elemental selectivity, linear response over a large dynamic range and very high sensitivity. The analysis consist of three steps: i) the solid sample is vaporized by laser ablation to form a plume of neutral atoms, ii) the neutral atoms of a specific atomic element in the plume are resonantly excited and ionized by another tunable laser source, finally iii) the ions created are mass analyzed in a time-of-flight mass spectrometer. The technique was developed at AMTEL for the mining industry for trace element analysis of Au, Pd, and Rh in rock minerals. The TOF-RIMS mass spectrometer was calibrated using NIST reference samples that provide trace concentrations of Au, Pd, and Rh within three decades of dynamic range. Detection limits attained, for the above mentioned elements are in the low ppb range.

9:40 AM INVITED PAPER
DETECTION OF SURFACE SPECIES ON SULPHIDE MINERAL GRAINS BY TIME OF FLIGHT SECONDARY-ION MASS SPECTROMETRY (TOF-SIMS): *Joo Y. Kim*[1]; Stephen Chryssoulis[2]; [1]Noranda Technology Centre, 240 Hymus Blvd., Pointe Claire, Quebec H9R 1G5 Canada; [2]Advanced Mineral Technology Lab (AMTEL), 100 Collip Circle, UWO Research Park, London, Ontario N6G 4X8 Canada

TOF-SIMS (time of flight secondary-ion mass spectrometry) was used to detect, identify and determine the types of species adsorbed on the surface of mineral grains obtained from the process streams of Brunswick concentrator. Lead on the surface of pyrite and sphalerite particles was detected and its distribution was mapped. Pyrite of the Pb-upgrading concentrate has comparable amount of surface lead wit the pyrite grains in the final tails. Sphalerite of the zinc concentrate and plant tails also have comparable surface lead. On pyrite surfaces, lead is more unevenly distributed. The only galena grains detected on the pyrite and sphalerite particles are unliberated remnants attached phases. The principal forms in which lead is lost in the Brunswick circuits are galena attached onto pyrite and halena in the size fraction of minus 5 microns. This accounts for 2/3 of the total lead content in the pyrite concentrate. The study demonstrated the ability of TOF-SIMS to detect the nature of surface species on the mineral particles and showed the technique as an excellent tool for establishing the surface compositions of minerals.

10:00 AM
THE USE OF CATHODOLUMINESCENCE MICROSCOPY AS AN ANALYTICAL TECHNIQUE IN THE MINERAL INDUSTRIES: *Richard D. Hagni*[1]; [1]University of Missouri-Rolla, Dept. of Geology and Geophysics, 125 McNutt Hall, Rolla, MI 65409-0410 USA

Cathodoluminescence Microscopy (CLM) is a valuable technique whose unique character and range of applications to problems in the mineral industries is not adequately recognized and appreciated. Many of the valuable non-metallic minerals exhibit strong cathodoluminescence that makes their recognition and study of grain size, shape, and distribution remarkably easy in exploration and mine samples. CLM forms an especially valuable tool in the analysis of beneficiation problems involving non-metallic ore and gangue minerals. CLM is often the best technique for the study of mineral textures in refractory and pyrometallurgical problems. CLM is an analytical technique that should be more wide used in the minerals industry.

10:20 AM BREAK

10:40 AM

ADVANCED MICROBEAM TECHNIQUES IN THE DETERMINATION OF GOLD MINERALOGICAL BALANCES: *Stephen L. Chryssoulis*[1]; *Stephen Knipe*[1]; [1]AMTEL, 100 Collip Circle, UWO Research Park, London, Ontario N6G 4X8 Canada

The accurate determination of the mineralogical distribution of gold is important in determining the metallurgical treatment of ores and in optimizing recovery. The mineralogical forms of gold and the microbeam techniques applied to their study include: (i) visible gold minerals which can be studied by electron probe (EPMA) to evaluate grain size, composition, and association; (ii) submicroscopic gold which can be quantified in sulphide and oxide minerals by SIMS; (iii) surface gold which may be detected and quantified by TOF-LIMS on a number of substrates (e.g.) carbonaceous matter, iron oxides, and sulphides; colloidal and fine gold associated with quartz and other gangue minerals for which PIXE is used and TOF-RIMS analysis is being developed. The study procedure, instrumentation, and data evaluation are discussed using representative examples from ores showing each form of gold.

11:00 AM

DETERMINATION OF QUANTITATIVE MINERALOGICAL BALANCES FOR MAJOR AND TRACE ELEMENTS: *Louis J. Cabri*[1]; William Petruk[1]; J. H. Gilles Laflamme[1]; [1]CANMET, MMSL, 555 Booth St., Ottawa, Ontario K1A 0G1 Canada

A quantitative mineralogical study using ore microscopy, electron microscopy, proton-microprobe, image analysis, and material balances was done on samples from the circuit of a mill in Québec, with particular emphasis on the Cu concentrate. The ore contains many different minerals, of which the principal ones, in decreasing order of abundance, are pyrite, sphalerite, chalcopyrite, bornite, galena, tennantite, and pyrrhotite. Minor to trace amounts of covellite, chalcocite, stannoidite, mawsonite, colusite, wittichenite, miharaite, hessite, petzite, electrum, and an unidentified Cu-Pb-Bi-sulfide also occur. Liberation of pyrite is very high in all size fractions for all samples (averages range from 80-91%). Liberation of chalcopyrite, bornite, sphalerite, and tennantite is relatively high, on average, in the head sample and Cu concentrate (58-74% and 66-88%, respectively). Most of the chalcopyrite in the flotation tails is not liberated, whereas about one half of the tennantite and sphalerite are liberated in both the flotation and final tails. Recoveries calculated for the Cu concentrate (on the basis of assays, mineralogy, and image analysis) are chalcopyrite 87.7%, bornite 67.5%, sphalerite 41.7%, tennantite 88.1%, galena (together with some trace minerals) 33.0%, pyrrhotite 26.2%, and pyrite 2.4%. Materials balance calculations, were done on the five major sulfide minerals, to determine the mineralogical distribution of 13 major, minor, and trace elements (as determined by proton-microprobe analyses). It was determined that, in the Cu concentrate, tennantite is the principal carrier of Bi (60%), As (83%), and Te (80%). Therefore, removal of tennantite, which is mostly liberated in the Cu concentrate (average 88%) would significantly reduce these three contaminant elements, but at a loss of 8% of the Cu, 1.9% of the Zn, and 0.6% of the Ag. The precious metals (Au, Ag) occur as discrete minerals (electrum, petzite, hessite); some of the Ag occurs in solid solution in bornite (19.4% of Ag in Cu concentrate) and in sphalerite. Four of the major sulfides (chalcopyrite, bornite, sphalerite, tennantite) in the ore also contain measurable concentrations of the following additional elements: Se, Cd, In, Sn, and Sb, occurring mostly as solid solutions. Some of these elements are also concentrated (up to ab out 18%) in minor and trace minerals such as colusite, stannoidite, and mawsonite.

11:20 AM

MINERALOGICAL TRANSFORMATION OF A COMPLEX CU-ZN CONCENTRATE DURING PARTIAL ROASTING IN A NICHOLS HERRESHOFF MONOHEARTH FURNACE: E. Boydens[1]; S. Brouwer[2]; *L. J. Evrard*[1]; E. Bosly[2]; [1]Université Catholique de Louvain, Dépt. des Sciences des Matériaux et des Procédés, PCIM, Place Sainte Barbe, 2, Louvain-la-Neuve 1348 Belgium; [2]Union Minière, UM Research, Kasteelstraat, 7, Olen 2250 Belgium

A partial desulphurization roasting process has been tested on a typical copper-zinc sulfide concentrate in a Nichols Herreshoff monohearth pilot furnace whereby the sulfur is partially removed and iron is to a certain degree preferentially oxidized. The phase changes that occur in the particles during selective roasting at 650°C and 800°C over a range of residence times were investigated by the use of chemical analysis, light microscopy, X-ray diffraction and electron microprobe analyses. The purpose of this work was to get an insight into the mineral assemblages by controlled oxidation roasting and to evaluate if this non traditional approach could be afterwards used to recover zinc, copper and iron by a physical separation method.

11:40 AM

CERAMIC MATRIX COMPOSITE ALUMINUM NITRIDATION MINERALOGICAL CHARACTERIZATION UTILIZING ELECTRON MICROSOCOPY, OPTICAL MICROSCOPY, AND X-RAY DIFFRACTION TECHNOLOGY: *Ann M. Hagni*[1]; [1]A. P. Green Refractories, Inc., Research Division, 1 Green Blvd., Mexico, MO 65265 USA

Ceramic matrix composites are inorganic materials that are particularly resistant to heat and abrasion. A magnesia (MgO) and aluminum nitride (AlN) based composite is formed by exposing a magnesia preform to a metallic alloy block in a nitrogen atmosphere at 950°C. The metallic alloy, which is composed primarily of aluminum, is wicked into the preform. Aluminum nitride matrix is grown between MgO particles as the wicked metallic aluminum reacts with nitrogen. Unused metallic alloy, remnant metallic alloy (carcass), and composite produced after 8 hours, 50 hours, and 225 hours of processing are characterized mineralogically. Reflected light microscopy, transmitted light microscopy, scanning electron microscopy, energy dispersive spectroscopy, and X-ray diffraction techniques reveal that in addition to anhedral to euhedral Al_3Ni, Al_2Si_2Sr, and Al crystallizing in the metallic alloy carcass, AlN and (Al,Si)N have formed as well. Nitride rings and nodules in the carcass may hinder AlN growth in the composite. Fine-grained residual Al_3Ni and Al_2Si_2Sr are dispersed throughout the composite matrix. The nitride matrix is composed of AlN and (Al,Si)N. Rim replacement of MgO by spinel occurs in the composite. Aluminum nitrides in the metallic carcass cathodoluminesce deep blue-purple, unlike non-luminescent AlN in the composite matrix. This distinction in cathodoluminescence suggests a different mode of formation for composite AlN than for carcass AlN. Phase interpretations and textural characterizations deduced from the implementation of sophisticated mineralogical techniques have contributed to the understanding, and will aid in the improvement, of MgO/AlN-based ceramic matrix composite processing.

CAST SHOP TECHNOLOGY: DC Casting/ Modeling 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

Wednesday AM Room: 6C
March 3, 1999 Location: Convention Center

Session Chair: Dr. James W. Evans, University at California, Berkeley, CA 94720 USA

8:30 AM
A MICRO/MACRO MODEL FOR THE EQUIAXED GRAIN SIZE DISTRIBUTION IN DC-CAST ALUMINIUM INGOTS: *Arild Hakonsen*[1]; Dag Mortensen[2]; Steinar Benum[1]; Hans Erik Vatne[1]; [1]Hydro Aluminium, R&D Materials Technology, P.O. Box 219, Sunndalsora, More & Romsdal 6601 Norway; [2]Institute for Energy Technology, Mats. and Corrosion Tech. Dept., P.B. 40, Kjeller, Akershus 2007 Norway

A micro/macro model for dendritic equiaxed grain nucleation and growth is applied on the DC-casting process of sheet ingots. Different nucleation laws, which all relates the nucleation to the undercooling of the melt, are compared. The growth velocity of the grain envelope is restricted by the alloying elements. The results of the micro model are the evolution of the solid fraction until impingement of the grains, as well as the mean grain size. The model is also able to calculate the grain size distribution around the mean size. The macro model for heat and fluid flow is coupled with the micro model by an iterative micro/macro time step scheme. This coupling makes it possible to calculate the grain size distribution versus position in the ingot. The modelling results are compared with measurements of secondary dendrite arm spacing and mean grain size in ingots with varying grain refinement additions.

8:55 AM
THERMOMECHANICAL BEHAVIOR OF AN AA3004 ALLOY AT LOW STRAIN RATE: *W. M. Van Haaften*[1]; B. Magnin[2]; W. H. Kool[1]; L. Katgerman[1]; [1]Delft University of Technology, Laboratory of Materials, Rotterdamseweg 137, Delft, 2628 AL The Netherlands; [2]Pechiney CRV, BP 27, Voreppe 38340 France

Recent thermomechanical modelling to calculate the stress field in industrially DC cast slabs has been successful, but lack of material data limits the accuracy of these calculations. The aim of this study is to determine the constitutive behaviour of AA3104 in as-cast condition. This was done by tensile testing at low strain rates in a broad temperature range. The parameters of a modified Ludwig equation were determined and are now being used in thermo-mechanical models. In order to study the material during later stages of casting, its behaviour at 50°C after prestraining at higher temperatures was also investigated.

9:20 AM
PHYSICAL MODELING OF THE EFFECTS OF THERMAL BUOYANCY DRIVEN FLOWS IN EM AND DC CASTERS: *D. Xu*[1]; [1]University of California - Berkeley, Dept. of Mats. Sci. and Mineral Eng., 516 Evans Hall, Berkeley, CA 94720 USA

Particle Imaging Velocimetry (PIV) was used to illustrate the role of thermal buoyancy driven flows in a laboratory scale model of an aluminum caster. The use of PIV enables the entire flow field to be captured at once yielding a quantitative description of the fluid. The water model, described in preceding papers, was equipped with a water heater than enabled preheated water to enter the system. The Tundish number, along with the Reynolds number, was matched with operational properties of an actual aluminum caster to obtain thermal and dynamic similarity. Results were obtained for representative superheats of 50, 75 and 100°C in two different combo bags and a channel bag. The results suggest that thermal buoyancy does modify the flow and is therefore important in proper representation of the actual system, however; the flow driven by the inflow through the nozzle/ bag system was still dominant in the sump.

9:45 AM
EFFECTS OF COMBO BAG GEOMETRY ON THE THERMAL HISTORY AND SUMP PROFILE OF A 3104 DC CAST INGOT: *W. K. Jones*[1]; D. Xu[1]; J. W. Evans[1]; E. Williams[1]; [1]University of California, Dept. of Mats. Sci. and Mineral Eng., 516 Evans Hall, Berkeley, CA 94720 USA

An experimental campaign was performed at the Reynolds Metals Company Cast House, Richmond, VA, to study the influence of combo bag geometry on a DC cast aluminum alloy. Two different size combo bags were chosen and subject to two different casting practices. Sacrificial thermocouples were used to track the steady state thermal history. The results clearly show that the longer bag created a deeper sump, up to four inches in the center. This is anticipated as previous experiments on a water model at Berkeley shows that the longer bag directs more aluminum into the lower regions of the sump. This result is important noting that previous research has shown a deeper sump to have greater centerline macrosegregation. A different set of stationary thermocouples was used to obtain the liquid temperature in an attempt to resolve the turbulent nature of the flow. The measurements showed that the shorter bag produced greater thermal fluctuations, which are believed to due to a greater level of turbulence. Fourier analysis was performed to determine the periodicity of the turbulence. Macrosegregation profiles were obtained across the rolling faces and the larger bag showed worse negative macrosegregation.

CAST SHOP TECHNOLOGY: Molten Metal Processing - Final Properties

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

Wednesday AM Room: 6D
March 3, 1999 Location: Convention Center

Session Chair: Dr. Ray D. Peterson, IMCO Recycling, Irving, TX 75039 USA

8:30 AM
PROCIAS: A JOINT PROJECT ON PROCESS CONTROL OF ALUMINIUM MELTS: *François De Schutter*[1]; Johan Verwimp[1]; Willy Engelen[1]; Stefan Kuypers[1]; Marc Ryckeboer[2]; Werner Verberckt[3]; Peter Hermans[4]; Cees Castelijns[5]; [1]Vlaamse Instelling Voor Technologisch Onderzoek, Boeretang 200, Mol 2400 Belgium; [2]Remi Claeys Aluminium NV, Kortemarkstraat 52, Lichtervelde B-8810 Belgium; [3]Hayes Lemmerz Belgium BVBA, Lage Weg 392, Hoboken B-2660 Belgium; [4]Lamitref Metals NV, Fr. Sheidlaan, Hemiksem B-2620 Belgium; [5]Hoogovens Aluminium NV, Stockletlaan 87, Duffel B-2570 Belgium

In order to ameliorate the current melting processes of the Flemish aluminium industry a joint project between a research institute and four foundries/cast houses was set up. The aluminium companies cover a large product area ranging from cast wheels, high frequency welded tubes, rolled electricity wire up to rolling slabs and extrusion billets for transportation, construction and engineering purposes. During the in-depth analysis of the industrial melts the chemical composition is monitored using optical emission spectroscopy, hydrogen concentration us-

ing the Alscan device and finally the qualitative as well as the quantitative inclusion concentration using the novel PoDFA-f and LiMCA-II. The aim is to make a coupling between melt parameters and the final material properties. In order to achieve this goal, several process parameters have been identified as important: material supply, temperature, fluxing, modifiers, degassing, grain refinement, metal velocity and filtering. The role of each of these parameters and their influence on the melt properties as well as the final end product properties will be investigated by modern design of experiment techniques. This paper will discuss the practical introduction of these techniques for these purposes as well as the introduction of the state-of-the-art measuring tools into the Flemish aluminium industry.

8:50 AM

SCRAP VARIABILITY AND ITS EFFECTS ON PRODUCING ALLOYS TO SPECIFICATION: *Ray D. Peterson*[1]; [1]IMCO Recycling, Inc., 5215 North O'Connor Blvd., Irving, TX 75039 USA

Historically, aluminum products were fabricated from prime metal and master alloys to achieve the desired final alloy composition. Today, many aluminum products are made entirely from scrap-based charges. Aluminum scraps are broken down into a myriad of subcategories based on source, alloy chemistry, and cleanliness. Yet there is still significant variability within a single scrap type. This degree of variability is different for various types of scraps. The variability also changes for different elements within a single scrap type. All of this variability in the scrap complicates the charge calculation and the subsequent manufacture of specification alloys. Sources of variability within a scrap type are discussed along with methods of characterizing the scrap. The implications of scrap variability and its effect on meeting specifications and determining production cost are considered.

9:10 AM

THERMODYNAMIC COMPUTER PROGRAMS AS AN AID IN REFINING OF ALUMINIUM: *Aud Nina Waernes*[1]; Johan Kr. Tuset[2]; Soeren Groenborg Hansen[2]; [1]SINTEF, Materials Technology, Alfred Getz v 2B, Trondheim N-7034 Norway; [2]Norwegian University of Science and Technology, Dept. of Metall., Alfred Getz v 2B, Trondheim N-7034 Norway

Computer Programs for calculation of complex chemical equilibrium is a powerful tool for solving problems in the metallurgical industry, for instance in refining of aluminium containing dissolved impurities. Since the refining process probably take place under conditions close to chemical equilibrium, modelling based on thermodynamic calculations is an important tool in optimising the process or when new processes are being planned. Most metallurgical processes and systems depend on the properties of solutions such as alloys, slags and salts. It is well known that when different substances are mixed, the resulting mixture often display properties different from those expected on basis of ideal mixing. Computer programs like ChemSage, include different solution models that describe the deviation from ideal mixing for alloy systems. In the refining of aluminium and aluminium alloys, knowledge of the interaction between both the dissolved impurity elements (Na, K, Ca, Li etc.) and the alloying elements are essential. This means that in order to achieve reliable results from the computer calculation, consistent thermochemical data must be available. By combining data from the literature with data from the databases that comes with the computer programs, equilibrium condition for the progress of the refining of aluminium with different fluxing agent (Cl2 and AlF3), has been calculated. The advantage of using a thermodynamic computer program in the calculation of the progress of aluminium refining is that the influence of temperature, amount of fluxing agents and alloy composition, on the final metal composition can very easily be established.

9:30 AM

SOLIDIFICATION STRUCTURES AND PROPERTIES OF CAST SAMPLES OF ZINC-ALUMINUM ALLOYS AND COMPOSITES: *Carlos Enrique Schvezov*[1]; Rafael Auras[2]; [1]University of Misiones, Faculty of Sciences, 1552 Azara St., Posadas, Misiones 3300 Argentina; [2]CONICET/UNSAM-CNEA, 1552 Azara St., Posadas, Misiones 3300 Argentina

Zinc-Aluminum alloys with different additions of Silicon and Copper and the respectives composite containing Silicon Carbides particles as reinforcements were cast in small samples. The cast alloys and composites were analysed using quantitative metallography and the size of the solidification structure were determined along with the particle size distribution in number and location. In addition, SEM analysis of the different alloying element distribution in the microstructure were performed in different sample positions which show different size structures. The Silicon precipitates were identified and their size and location determined. The samples were tested for hardness and wear. The hardness values were correlated with the local structure, alloy composition and particle distribution. The wear tests were performed at different pressures and speeds. The results of this investigation will be presented and discussed. Particular attention is given to the correlation between the microstructure and the mechanical properties which can be employed to improve the use of these alloys.

9:50 AM

A THERMODYNAMIC DATABASE ON ALUMINUM ALLOYS FOR PRACTICAL ALLOY DESIGN: *Haiyan Liang*[1]; Y. Austin Chang[1]; [1]University of Wisconsin-Madison, Dept. of Mats. Sci. and Eng., 1509 University Ave., Madison, WI 53706 USA

A thermodynamic database has been developed for multicomponent aluminum alloys. All the major alloying elements used in commercial aluminum alloys have been included in this database. By integrating the thermodynamic database with kinetic solidification models we can predict solidification paths of commercial aluminum alloys. In this presentation, we report the model-calculated solidification paths for several alloys with compositions close to real commercial aluminum alloys. The calculated results are in good agreement with experimental data reported in the literature. To further confirm the reliability of the database, our group performed detailed experimental investigations on the microstructure and microsegregation of the Al-Cu-Mg-Zn quaternary alloys. The experimental results are in accord with calculations. The good agreement obtained between calculations and experiments demonstrated that the thermodynamic database can be used for practical alloy design to achieve desired microstructures and properties for commercial alloys.

10:10 AM BREAK

10:30 AM

ELEMENT DISTRIBUTION IN Al-Si ALLOYS: *Heng-Xian Zhao*[1]; Xiao-Fei Xu[1]; [1]Northeastern University, Shenyang 110006 China

Investigation on element distribution in Al-Si alloys has been made. A number of ingot samples were analyzed using a Foundry Spectrovac (FSQ,BAIRD,USA). The contents of some elements are found different in different zones of the ingots. Discussion and conclusion are given in the paper.

10:50 AM

PREPARATION OF Al-Si ALLOYS USING SODIUM- FLUOSILICATE AND MOLTEN ALUMINIUM: *Ibrahim Hamed Aly*[1]; A. A. Nofal[2]; E. E. Ebrahiem[1]; F. M. Ahmed[3]; A. M. Omran[3]; [1]Minia University, Chem. Eng. Dept., Faculty of Engineering, El-Minia Egypt; [2]Central Metallurgical Research and Development Institute, President, El-Tebbin Egypt; [3]Aluminium Company of Egypt, Nag-Hammady Egypt

Al-Si alloys, and sodium aluminium fluorides were produced by reacting molten pure aluminium with sodium fluosilicate (by-product from super-phosphate fertilizer plants). The obtained products can be easily separated and used directly in casting shops or aluminium reduction cells in aluminum smelters. The produced Al-Si alloys are high quality, containing up to 20% silicon and less than 0.12% iron. Different factors affecting the composition of the produced Al-Si alloys were studied. These factors are: temperatures, mixing intensity, sodium fluosilicate to aluminium ratio, feeding rate and particle size. The results obtained were correlated and empirical equations representing the silicon-content in the produced alloy with each factor. Microstructure examination and x-ray diffraction were carried out on the produced alloys as well as the fluorine salts.

11:10 AM

MICROSTRUCTURES AND ELECTRICAL PROPERTIES OF STRONTIUM TREATED ALUMINUM FOUNDRY AND WROUGHT

ALLOYS: *B. Closset*[1]; [1]Timminco, 44, Chemin Petite-Boissiere, Geneve CH-1208 Switzerland

Aluminum foundry and wrought alloys treated with strontium were examined by optimal microscopy. It is shown that strontium affects mainly the eutectic silicon in Al-Si foundry alloys and to a lesser extend other compounds such as Mg2Si and AlFeSi. In wrought aluminum 6XXX series the strontium addition results in a change of morphology of the ternary AlFeSi intermetallics. The shape of coarse - AlFeSi is altered and a more finely dispersed - AlFeSi intermetallics are obtained. The electrical resistivity or conductivity of both types of aluminum alloys were measured before and after strontium treatment Strontium modified Al-Si foundry alloys exhibit a higher electrical conductivity. It has also been demonstrated that the strontium treated alloys react differently to a heat treatment cycle (T4 or T6) than unmodified alloys. In this work microstructural changes are correlated to electrical resistivity or conductivity measurements.

11:30 AM

DISSOLUTION MECHANISMS OF COMPRESSED ADDITIVES IN ALUMINIUM: *David John Bristow*[1]; Sarah Lockwood[2]; Tom Woodcock[2]; Ray Cook[1]; [1]London & Scandinavian Metallurgical Company, Ltd., Technical Centre, Fullerton Rd., Rotherham, S. Yorks S60 1DL UK; [2]University of Sheffield, Dept. of Eng. Mats., Mappin St., Sheffield, S. Yorks S1 3JD UK

The addition of compressed powder additives to aluminium for alloying purposes is well established. In this investigation, the mechanisms by which tablet dissolution occurs, and the reasons for variable rates of dissolution have been investigated. The dissolution of additives containing Cr, Fe, Mn and Ti have each been investigated, by quenching the aluminium at various times after tablet addition. Tablet disintegration is monitored, and metallography reveals the successive phases which develop. These are related to the diffusion rates of species through the successive layers of intermetallics. Fe-based additives are shown to exhibit a tabletting pressure sensitivity whose practical implications are discussed.

CREEP BEHAVIOR OF ADVANCED MATERIALS FOR THE 21ST CENTURY: Low Stress Creep Mechanisms: A Discussion I

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 USA; Amiya K. Mukherjee, University of California, Dept. of Chem. Eng. & Mats. Sci., Davis, CA USA; K. Linga Murty, North Carolina State University, Box 7909, Raleigh, NC 27695-7909 USA

Wednesday AM Room: 15A
March 3, 1999 Location: Convention Center

Session Chair: B. Dyson, Imperial College of Science, London, England; M.J. Mills, Ohio State University, OColumbus, OH USA

8:30 AM INTRODUCTION

8:35 AM KEYNOTE

PARTICLE DISTRIBUTION AFTER DIFFUSIONAL CREEP: *F. R. N. Nabarro*[1]; [1]Division of Materials Science and Technology, CSIR, PO Box 395, Pretoria 0001 and, Condensed Matter Physics Research Unit, University of Witwatersrand, Private Bag 3, Wits 2050, Johannesburg South Africa

The theory of diffusional creep implies that in a particle-strengthened alloy there will be zones denuded of particles on grain boundaries transverse to a tensile stress and zones enriched in particles on lateral boundaries. Within this framework, Bilde-Sorensen, Smith and Thorsen have studied the complications which arise when one considers both the glide and the climb forces on dislocations in the grain boundaries. Ruano, Sherby, Wadsworth and Wolfenstine have argued that the presence of denuded zones is not conclusive evidence for diffusional creep, and have proposed two other mechanisms. We argue here that one mechanism, the dragging of particles by a migrating boundary will produce an enriched zone immediately adjacent to the denuded zone, and cannot account for isolated enriched and denuded zones, while the other mechanism, re-solution of the particles, is implausible and cannot account for enriched zones.

9:05 AM KEYNOTE

DEFORMATION MECHANISMS IN CRYSTALLINE SOLIDS AND NEWTONIAN VISCOUS BEHAVIOR: *Oleg D. Sherby*[1]; Oscar A. Ruano[2]; Jeffrey Wadsworth[3]; [1]Stanford University, Dept. of Materials Science and Engineering, Stanford, CA 94305 USA; [2]CENIM, CSIC, Dept. of Phys. Metall., Av. Gregorio del Amo 28040 Spain; [3]Lawrence Livermore National Laboratory, P.O. Box 808, L-353, Livermore, CA 94550 USA

The three principal mechanisms of plastic flow in crystalline solids at elevated temperature are crystal slip, grain boundary sliding and diffusional flow. All these mechanisms involve the diffusion of atoms as the rate controlling process, either in the lattice or in the grain boundary. Under the correct condition of microstructure, temperature and stress, each mechanism can lead to Newtonian-viscous flow behavior. That is, the strain rate increases linearly with the applied stress. In the case of crystal slip, Newtonian-viscous behavior is observed at very low stresses, and, in pure metals, is known as Harper-Dorn (H-D) creep. It is also observed in anisotropic crystalline solids when deformed under thermal cycling conditions. The dislocation density and the stacking fault energy are important structural factors that contribute to crystal slip-controlled Newtonian flow. In the case of grain boundary sliding, Newtonian -viscous behavior is observed in fine-grained solid solution alloys under conditions where grain-boundary sliding is accommodated by dislocation glide controlled by the diffusion of solute atoms. In the case of diffusional creep, which is rigorously described by the Nabarro-Herring (N-H) theory, the creep rate is controlled by grain size and by the rate of atom diffusion in the lattice and in the grain boundary. Deformation mechanism maps permit establishing the conditions of dislocation density, grain size, stress and temperature where each deformation process can be expected to be rate-controlling.

9:35 AM KEYNOTE

THE IDENTIFICATION AND SIGNIFICANCE OF DIFFUSIONAL CREEP PROCESSES: *G. W. Greenwood*[1]; [1]University of Sheffield, Dept. of Engineering Materials, Sheffield S1 3JD UK

The theory of diffusional creep was first put forward 50 years ago and the physical basis of the theory has never been disputed. It provides equations that predict creep rates in terms of parameters that can separately be determined. Whilst several experimental studies have supported the theory, others have illustrated situations where these equations do not apply. Such results have led to proposals that this form of creep does not occur or that, in some situations, the original theory requires modification. In the present paper attention is particularly given to identifying the conditions under which this form of creep may predominate and the relationships that are then applicable. The validity of the original theory requires that lattice dislocations remain immobile and that grain boundaries act as perfect sources and sinks for vacancie and do not undergo Rachinger type sliding. It is now established that microstructural features can be important and specific microstructural changes, including grain size and shape, precipitate location and grain boundary profiles can be observed. These can influence the time, temperature and stress dependence of strain. Below specific temperatures grain boundary diffusion coefficients are important and can be highly sensitive to impurities. Some appreciation can be obtained of the transition from diffusional to dislocation creep through a knowledge of the patterns of variation of internal stress. Finally, the importance of

identifying the mode of deformation and the part that may be played by directional diffusion are shown to be of crucial significance in understanding mechanisms of fracture at elevated temperatures, in radiation damage and in joining and sintering processes as well as in diffusional creep.

10:05 AM INVITED PAPER
DEFORMATION BY GRAIN BOUNDARY SLIDING AND SLIP CREEP VERSUS DIFFUSIONAL CREEP: *Jeffrey Wadsworth*[1]; Oscar A. Ruano[2]; Oleg D. Sherby[3]; [1]Lawrence Livermore National Laboratory, P.O. Box 808, L-353, Livermore, CA 94550 USA; [2]CENIM, CSIC, Dept. of Physical Metallurgy, Av. Gregorio del Amo 28040 Spain; [3]Stanford University, Dept. of Materials Science and Engineering, Stanford, CA 94305 USA

A review is presented of the debates between the present authors and other investigators regarding the possible role of diffusional creep in the plastic flow of polycrystalline metals at low stresses. These debates are recorded in eleven papers over the past seventeen years. in these papers it has been shown that the creep rates of materials in the so-called "diffusional creep region" are almost always higher than those predicted by the diffusional creep theory. Additionally, the predictions of grain size effects and stress exponents from diffusional creep theory are often not found in the experimental data. Finally, denuded zones have been universally considered to be direct evidence for diffusional creep; but, those reported in the literature shown to be found only under conditions where a high stress exponent is observed. It is proposed that diffusion-controlled dislocation creep is the dominant deformation process during the formation of such denuded zones by stress-directed grain boundary migration with the precipitates dissolving in the moving grain boundaries. The above observations have led us to the conclusion that grain boundary sliding and slip creep are the principal mechanisms for plastic flow in the so-called "diffusional creep regions."

10:30 AM BREAK

10:40 AM INVITED PAPER
EVIDENCE FOR DIFFUSIONAL CREEP IN Cu-2wt%Ni: *J. B. Bilde-Sørensen*[1]; P. A. Thorsen[1]; [1]Risø National Laboratory, Materials Research Dept., Roskilde DK-4000 Denmark

A sample of Cu-2wt%Ni was crept in tension to an elongation of 2.4% at 1073 and 1103 K under a stress of 1.14 MPa. Prior to creep the sample was covered with a regular grid of alumina. After creep the local deformation could be measured from the grid. The deformation was seen to be localized to the boundaries. With a knowledge of the orientation of the grain boundary plane the deformation can be divided into a sliding component and a component arising from removal or deposition of material at the boundary. It was demonstrated that material had been deposited at some of the transverse boundaries and removed from some of the longitudinal boundaries. The results are discussed in terms of the coincident site lattice (CSL) model for the grain boundary structure. On this basis it is possible to explain a number of features that have all been observed experimentally: (i) some boundaries close to an exact CSL orientation are inactive, (ii) the ratio of sliding to deposition/removal varies from boundary to boundary, (iii) some transverse boundaries exhibits negative climb (iv) material is deposited on some of the longitudinal boundaries. It is suggested that contemporary grain boundary theory should be included in a revised model for diffusional creep.

11:05 AM INVITED PAPER
CASE STUDIES IN DIFFUSIONAL CREEP: *Brian Wilshire*[1]; [1]University of Wales, Swansea, Materials Engineering, Singleton Park, Swansea, Wales SA2 8PP UK

Diffusional creep theories are undoubtedly elegant and have been widely assumed to account for the high temperature creep behaviour displayed by many metallic and ceramic materials at low stresses. However, the experimental observations commonly quoted as evidence for diffusional creep are, at best, inconclusive. The limitations of this evidence are reviewed for pure metals and particle-strengthened alloys, as well as for monolithic ceramics and ceramic-fibre-reinforced ceramic matrix composites.

11:30 AM
A FINITE ELEMENT STUDY OF GRAIN BOUNDARY SLIDING IN INCANDESCENT LAMP FILAMENTS: *John Selverian*[1]; [1]Osram Sylvania Development Inc., 71 Cherry Hill Drive, Beverly, MA 01915

Finite element analysis was used to study the effect of grain boundary creep on sag and kinking of incandescent lamp filaments. Grain boundary creep can explain most of the sag and kinking seen in standard filaments. As the number of grain boundaries increase the amount of sag increases. As the degree of grain boundary interlocking decreases the sag increases. Kinks can be explained by grain boundaries with a low degree of interlocking, i.e. flatter. Not every flat grain boundary kinks. Kinks result whenever there are a few grain boundaries that are significantly flatter (by approximately a factor of 3 than the majority of grain boundaries.

ELECTRICAL AND THERMAL PROPERTIES OF MATERIALS: Session I

Sponsored by: Electronic, Magnetic & Photonic Materials Division, Electronic Packaging and Interconnection Materials Committee
Program Organizers: Sungho Jin, Lucent Technologies Bell Labs, Murray Hill, NJ 07974 USA; Anthony Mulligan, Advanced Ceramics Research, 851 East 47th St., Tuscon, AZ USA; King Ning Tu, University of California, Dept. of Mats. Sci. and Eng., Los Angeles, CA 90095 USA

Wednesday AM Room: 16B
March 3, 1999 Location: Convention Center

Session Chair: K. N. Tu, University of California, Dept. of Mats. Sci. and Eng., Los Angeles, CA 90095 USA

8:30 AM INVITED PAPER
CONTACT ISSUES FOR GaN TECHNOLOGY: D. Qiao[1]; *S. S. Lau*[1]; [1]University of California, Dept. of Elect. and Computer Eng., San Diego, CA 92093-0407 USA

In this presentation, we review the metal-GaN contact technology to shed light on some of the critical issues such as GaN surface cleaning before metallization, low-resistance contacts to GaN/AlGaN hetero-structures, barrier heights of metals on AlGaN and on hetero-structures. Some general conclusions are drawn on the electrical behaviour of contacts for further advances in this field.

9:00 AM INVITED PAPER
MICROSTRUCTURE AND THERMOELECTRIC PROPERTIES OF SINTERED Bi2Te3: Gil-Geun Lee[1]; Byoung-Kee Kim[1]; *Hyung-Sik Chung*[1]; [1]Korea Institute of Machinery and Materials, Chanwon 641-010 Korea

Thermoelectric materials have been studied to increase the figure of merit by controlling of microstructure using powder metallurgical process. Various kinds of Bi2e3 starting powders which have different particle size distribution and second phase content are synthesized by mechanical grinding process, and their powders are sintered. The sintered bodies have shown different microstructure and characteristics, i.e.: grain size distribution and thermal/electric conductivity, etc.. This paper discusses the effect of microstructure on the thermoelectric properties of Bi2Te3 based on the effective medium and percolation theories.

9:30 AM
SEEBECK EFFECT ON AMORPHOUS-CRYSTALLINE INTERFACE AND AMORPHOUS-CRYSTALLINE THERMOCOUPLE: *Mikhail V. Finkel*[1]; Jim S.-J. Chen[2]; [1]DAATH-Scientific Center, Dept. of Mats. Sci., 9926 Haldeman Ave., #36A, Philadelphia, PA 19115 USA;

[2]Temple University, Mechanical Engineering Dept., Norris & 12th St., Philadelphia, PA 19022 USA

Seebeck phenomenon of an amorphous-crystalline interface has been discovered and studied for various alloy systems. Thermocouples consisting of amorphous and crystalline parts of a single alloy composition were created. A thermocouple made of as-cast Co-Fe-Si-B metallic glass demonstrates constant thermopower of 8.1mV/K in the temperature range from 293 to 593K. It has been shown that amorphous-crystalline thermocouple (ACT) can be stabilized by high-temperature anneal. Several methods are proposed for ACT fabrication. One of them involves crystallization of amorphous ribbon on the part of its length using heterogeneous temperature field. Sharp natural amorphous-crystalline transition zone plays a role of the thermocouple hot junction. It is suggested that for low and moderate temperatures ACT could be techni cally and economically more advantageous than traditional crystalline thermocouples.

9:50 AM

THE APPARENT ACTIVATION ENERGY AND CURRENT DENSITY EXPONENT OF ELECTROMIGRATION DAMAGE IN CHIP LEVEL INTERCONNECT LINES: A GRAIN STRUCTURE BASED STATISTICAL APPROACH: *T. M. Korhonen*[1]; Y. -K. Liu[1]; D. D. Brown[2]; M. A. Korhonen[1]; C. -Y. Li[1]; [1]Cornell University, Dept. of Mats. Sci. and Eng., Ithaca, NY 14583 USA; [2]Advanced Micro Devices, Sunnyvale, CA 94088 USA

Electromigration reliability assessment of chip-level interconnects is based on accelerated testing at a higher temperature and larger current density that expected in service conditions. The critical parameters needed to extrolate accelerated test data to service conditions are the activation energy, Q, and the current density exponent, n. Although these are well-known for the elemental processes there is no consensus which apparent activation energy or currently density exponent values would be appropriate in reliability estimates for realistic line structures comprising regimes of bamboo and polycrystalline sections. In this contribution we shall apply a Monte-Carlo approach to generate realistic-like ID line structures, and model their electromigration (EM) lifetimes. For a given grain structure distribution, we follow the stress evolution along the interconnect line and let a void nucleated at the growth of nucleated voids as a function of time until the largest of them reaches a specified size, resulting in a 'failure' of the particular line. By repeating this process for various temperatures and current densities we can extract the apparent activation energies and current density exponents from the modelling data. The results obtained compare well with literature data and prevalent theoretical concepts.

10:10 AM BREAK

10:30 AM INVITED PAPER

PATTERN FORMATION BY METALLIC AND NON-METALLIC MICROSPHERES IN A PASSIVE FLUID UNDER ZERO OR APPLIED FIELDS: *Weijia Wen*[1]; K. N. Tu[1]; [1]UCLA, Dept. of Mats. Sci. & Eng., Los Angeles, CA 90095-1595 USA

Electric-field-induced fractal and chain patterns formed respectively by metallic and non-metallic microspheres in silicone oil have been investigated. The two patterns are interchangeable if we start with the same glassy microspheres and coat them sequentially with metallic and by surface conductivity of the microspheres. Under zero field, Ni-coated glassy microspheres tend to form rings and chains. The ring and chain formation can be simulated on the basis of dipole-dipole interaction, without thermal noise, between microspheres.

11:00 AM

ELECTRICAL RESISTIVITY CHANGES AND PHASE TRANSFORMATIONS IN Ti-(25-52) AT.% Al ALLOYS: D. Veeraraghavan[2]; Uwe Pilchowski[1]; *Vijay K. Vasudevan*[1]; [1]University of Cincinnati, Dept. of Mats. Sci. & Eng., Cincinnati, OH 45221-0012 USA; [2]VLSI Technology, 9651 Westover Hills Blvd., San Antonio, TX 78251 USA

Phase transformations in Ti-(25-52) at.% Al were studied by electrical resistivity measurements over a range of temperatures using a special device. The alpha2, alpha, beta and gamma phases were observed to have distinctly different resistivities and temperature dependencies, owing to which phase transformations could be monitored. The room temperature resistivity of stoichiometric alpha2-Ti3Al and gamma-TiAl are 118 and 31 micro-ohm.cm, with a difference of 87 micro-ohm.cm. The changes in resistivity with temperature are also significantly different in that in alpha2 the resistivity saturates to a near-constant value near 750Ɣ, whereas that of the gamma phase shows a linear and near-constant slope with temperature like most metallic materials. In order to explain these differences, the electrical resistivity of alpha2 and gamma phases has been modeled by fitting the data using the Bloch-Gruneisen formulation with certain simplifying assumptions. Good agreement between the calculated and experimental resistivity-temperature curves, and between calculated and experimental values of residual resistivity and Debye temperature, were obtained. From the model, parameters such as Fermi velocity, effective mass of a conduction electron, the number of electrons participating in conduction and electron mean free path have been calculated for the two phases. The calculations reveal that the mean free path is of the order of the lattice parameter in the case of alpha2, which leads to high resistivity and resistivity saturation. The resistivity of the alpha2 phase is also higher than that of the gamma phase due to the fact the Fermi velocity of the electrons is lower, effective electron mass higher and fewer electrons participitate in conduction. These factors, coupled with hybridization and localization effects, cause the different electrical resistivity behavior of the two phases.

11:20 AM

THE EFFECT OF IMPURITY ON THE MECHANICAL AND THE ELECTRICAL PROPERTIES OF Cu-Cr IN SITU COMPOSITE: *Eiju Takakura*[1]; Kuniteru Mihara[2]; Hirowo G. Suzuki[1]; [1]National Research Institute for Metals, Materials Processing Division, 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047 Japan; [2]The Furukawa Electric Company, Ltd., Metal Research Center, No. 5 Research Section, 500 Kiyotaki, Nikko, Tochigi 321-1493 Japan

Cu-15wt%Cr in situ composite that has high strength and high electrical conductivity was developed, but it was not still economical because of its high purity ingredients. Lowering purity of ingredients is one of the candidates to decrease the production costs. In this study, we investigate the effect of impurity on the mechanical and the electrical properties of Cu-Cr in situ composite using two nine level of purity ingredients. Main impurity was Fe and it was scavenged into the Cr fiber. Vickers hardness of the cold drawn low purity material was 10Hv higher than the high purity one. This can be attributable to the hardening of Cr fiber. The electrical conductivity of the low purity material was almost the same as of the high purity one. It was clarified that the low purity materials can be utilized as the ingredient for the composite.

FLUID-FLOW PHENOMENA IN METALS PROCESSING: Metals Extraction and Smelting

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

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

Session Chairs: Hong Yong Shon, University of Utah, Salt Lake City, UT 84112-1183 USA; Stavros A. Argyropoulos, Dept. of Metall. and Mats. Sci., Toronto, Ontario M5S 3E4 Canada

8:30 AM
STUDY ON COMBUSTION OF BURNERS IN BLAST FURNACE STOVES: *Youduo He*[1]; [1]Baotou University of Iron & Steel Tech., Baotou, Inner Mongolia 014010 P.R. China

Burners are very important facilities for blast furnace stoves to raise hot-blast temperature up to 1200°. Nowadays, since the fuel being combusted in stoves is blast furnace gas only, to provide a suitable length of flame in combustion chambers of stove is drawing more attention. The length of flame should satisfy that the location of highest temperature of flue gas after full combustion is in the dome. The length of flame must be not too long so that part of the gas combustion does take place in upper part of checkerwork which will cause damage, subside and displacement of that part of checkerwork. Since the heat content of blast furnace gas is going down and the volume of gas passed through the burner become very large, the over long length of flame is often happened in practice. The length of flame should also not be too short because very large temperature gradient will cause large heat stress and the life of chamber wall be shorter. The turbulent diffusion flame of ceramic burners were simulated by three dimensional turbulent combustion programs, Which contained two equation models for turbulence, mixture fraction f and concentration fluctuation g for diffusion flame. Three kind of ceramic burners has been studied. They were common type of two rings (one ring linked with another), Hoogovens and a new burner designed by us. The flow pattern, the concentration and temperature distributions, the shape of flame, and the average length of flame with different conditions have been obtained. Some useful results can be extracted for practice. Besides, a pilot experiment of the new burner has been carried out at situ of Anshan Steel Complex to compare with the simulation results. The new ceramic burner has been accepted by Anshan Steel Complex and will put in practice at blast furnace number 4 which has 1000 cubic meters of working volume at the end of this year.

8:50 AM
MODELLING GAS INDUCED CONVECTION IN ALUMINA REDUCTION CELLS: *Knut Halvard Bech*[1]; Pål Tetlie[1]; *Asbjørn Solheim*[1]; *Torstein Haarberg*[1]; [1]SINTEF, Materials Technology, Alfred Getz vei 2b, Trondheim N-7034 Norway

Experiments were conducted in a water model of a two-dimensional (2D) section of a typical reduction cell. The metal-bath interface was modelled by a solid, non-deformable surface, so that convection was restricted to the "bath" (water) phase. Nitrogen gas flowed through a semi-permeable membrane under the model anodes, inducing an approximately two-dimensional circulation pattern in the side channel. The mean velocities and fluctuations were measured applying Laser Doppler Velocimetry. Side channel width, bath height and total gas flow rate were varied between the different experiments. A computer model of the experimental setup was established in the computational fluid dynamics (CFD) program Fluent. The bubbles were modelled as discrete, buoyant particles. However, due to the strongly localized momentum transfer and some physical shortcomings in the Fluent model, an adapted version of the program was constructed, incorporating the following changes: 1) The mass middle point of the bubbles were forced to at a distance away from the anode due to a repelling potential. 2) The momentum transfer was distributed over a region corresponding to the anticipated bubble size. 3) The momentum transfer was reformulated, ensuring conservation of momentum. The modified model reproduced the experimental data both qualitatively and quantitatively, except in narrow channels (10 cm width), where the real bubbles are of the same size as the channel width. After verifying the CFD model for the 2D flow situation, the model was applied in 3D computations, predicting the steady state flow around and between prebaked anodes. Results from the 3D model computations are presented.

9:10 AM
APPLICATION OF A REACTING CFD MODEL TO DROP TUBE KINETICS AND SMELTER SIMULATIONS: *B. R. Adams*[1]; K. A. Davis[1]; M. P. Heap[1]; A. F. Sarofim[1]; G. A. Eltringham[2]; A. A. Shook[2]; [1]Reaction Engineering International, 77 West 200 South, Suite 210, Salt Lake City, UT 84101 USA; [2]BHP, 7400 North Oracle Rd., Suite 200, Tucson, AZ 85704 USA

This paper discusses the use of a reacting CFD model to determine chalcopyrite kinetics in a drop tube furnace and to predict the reaction of a chalcopyrite concentrate in the reaction shaft of an industrial smelter. Drop tube furnaces are commonly used to derive kinetic parameters on pyrolysis and oxidation of different grade ores, since they can provide well-defined temperatures, oxygen concentrations, and residence times. For injection of particles at very low concentrations the gas concentration and temperature are not appreciably affected by the injected particles. Only in-furnace optical observations via pyrometry or high-speed photography or analysis of extracted particles by electron microscopy can be conducted at mass flow rates which are low enough to neglect perturbations of the gas temperature or concentration. At the higher concentrations needed for chemical or instrumental analysis, significant perturbations of the composition and temperature of the gas in the drop tubes can be expected. For such cases, reacting CFD codes can be applied to determine the consequences of the interaction of gas with particles and therefore improve the ability to derive kinetic parameters that take into account the different temperature and oxidation histories that different particles will see. This paper describes the application of such a model to derive improved kinetic parameters for the pyrolysis and oxidation of chalcopyrite. The improved kinetic parameters derived from the drop tube studies are then used to simulate chalcopyrite concentrate reactions in the reaction shaft of an industrial smelter. The reaction shaft model includes the effects of turbulent fluid mechanics, entrained flow mixing, turbulent particle dispersion, heterogeneous particle reactions, radiative and convective heat transfer, and surface and bath deposition rates. Particle reaction and composition characteristics are predicted as a function of particle trajectory and deposition and are used to aid in evaluating shaft performance.

9:30 AM
A 3-D COMPUTER MODEL OF THE FLASH CONVERTING FURNACE SHAFT: *Perez-Tello Manuel*[1]; *Hong Yong Sohn*[2]; Philip John Smith[1]; Kirsi M. Riihilahti[2]; [1]University of Utah, Dept. of Chem. and Fuels Eng., Salt Lake City, UT 84112 USA; [2]University of Utah, Dept. of Metallurgical Engineering, 412 William Browning Building, Salt Lake City, UT 84112 USA

A three-dimensional computer model for the Kennecott-Outokumpu flash converting process for copper matte is presented. The model incorporates the transport of momentum, heat, mass, and reaction kinetics between the gas and particles in a particle-laden turbulent gas jet. The standard k-e model is used to describe gas-phase turbulence in an Eulerian framework. The particle-phase is treated from a Lagrangian

viewpoint which is coupled to the gas-phase through the source terms in the Eulerian gas-phase governing equations. Matte particles were represented as Cu2S.yFeSx. Based on experimental observation, the oxidation products were assumed to be Cu2O, CuO, Fe3O4, and SO2. A reaction mechanism involving the external mass transfer of oxygen to the particle surface and diffusion of the oxygen through the oxide layers of Cu2O/Fe3O4 and CuO/Fe3O4 is proposed. Predictions of the computer model were compared with the experimental data collected in a large laboratory furnace. A reasonable agreement between the model predictions and the measurements was obtained in terms of fractional conversion of the oxidation reactions and of sulfur remaining in the reacted particles. The simulation of an industrial flash converting furnace was also performed. Higher oxidation rates, more even distribution of particles, and thus a more efficient use of the reactor volume are predicted with a burner having a distributor cone, than with a single-entry burner.

9:50 AM

MODEL STUDY ON DISPERSED-PHASE HOLDUP IN FERROALLOY REFINING PROCESSES: *G. Akdogan*[1]; B. Yoruc[1]; R. H. Eric[1]; [1]University of the Witwatersrand, School of Process and Materials Engineering, Private Bag 3, Johannesburg, Wits 2050 South Africa

An experimental study has been performed to investigate the dispersed phase holdup induced by a high-strength submerged gas injection in a bottom blown air-stirred one-seventh water model of CLU (Creusot-Loire Uddeholm) reactor usine two different tuyere configurations. The air flow rates varied from 0.00599 m3/s to 0.01312 m3/s. In these series of experiments, water height and kerosene height were kept constant at 0.23m and 0.02m respectively. The dispersed phase holdup was determined at various gas flow rates and nozzle orientations. The dispersed phase holdup increased with gas injection rate and decreased with vertical distance from the original interface. At a constant vertical distance, the radial distribution of the holdup was found to increase with increasing gas flow rate. At constant vertical distance and gas injection rate the dispersed holdup increased with increasing radial distance from the centerline. At constant gas flow rate, as the vertical distance increased in the centeline, off-center orientation of nozzles displayed higher values of the dispersed phase holdup than those of the center configuration. The variation of percentage of dispersed phase holdup with respect to vertical radial distances was also discussed in terms of the swirling action of the bath. The maximum dispersed phase holdup of 22% was achieved at the interface (vertical distance of zero) with a radial distance of 5cm from the centerline using 0.01081m3/s gas flow rate for off-center configuration of the nozzles. The minimum dispersed phase holdup of 3.64% was seen at a vertical distance of 0.22m from the interface with a radial distance of 10cm from the centerline at a flow rate of 0.00599m3/s for center configuration of nozzles.

10:10 AM BREAK

10:30 AM

FLOW VISUALIZATION AND TEMPERATURE MEASUREMENTS CLOSE TO THE ARC ATTACHMENT ZONE OF A LABORATORY SCALE DC FURNACE FOR SLAG CLEANING: *Adrian Christian Deneys*[1]; David G. C. Robertson[1]; [1]University of Missouri - Rolla, Center for Pyrometallurgy, 215 Fulton Hall, Rolla, MO 65409-1460 USA

Documentation of fluid flow phenomena on the surface of a molten slag have been made using video photography in a laboratory scale D.C. arc furnace. In addition, temperatures have been measured close to the D.C. arc attachment zone. A molybdenum thermocouple (with a 90Ɣ bend, 50 mm from tip) was inserted under the electrode, 5-30 mm below the surface of the molten slag bath. Two other temperatures were simultaneously measured; one submerged approximately 70 mm in the bath, against the crucible wall, and another 5-10 mm below the surface of the bath (also against the crucible wall). Initially induction heating melted approximately 2 kg of nickel flash smelter slag which has a liquidus temperature around 1150Ɣ. Transient temperature measurements were then obtained during discrete periods with the plasma arc turned on. Temperatures (and rates of temperature rise) were found to be a function of the depth of the thermocouple in the bath. As the depth decreased, the peak temperatures increased. With 3.3 kW of D.C. arc power supplied for 35 seconds (and the bent molybdenum thermocouple submerged 10 mm beneath the surface). The temperature under the electrode tip rose from 1181Ɣ to 1302Ɣ in 45 seconds. At the same power level, the temperature stabilized at 1420Ɣ on the surface of the bath (at the wall). Directly below the electrode (10mm beneath the slag surface), the temperature stabilized at 1398Ɣ. This work has been conducted to quantify the temperatures, fluid flow and reductant behavior present in the arc attachment zone of a D.C. arc furnace, and has relevance to optimizing furnace design for pyrometallurgical slag cleaning processes. A description of the experimental apparatus and experimental results will be presented.

10:50 AM

FLUID FLOW MODELING IN ELECTRIC ARC FURNACES: L. P. Gu[1]; *G. A. Irons*[1]; [1]McMaster University, Dept. of Mats. Sci. and Eng., 1280 Main St. West, Hamilton, Ontario L8S 4L7 Canada

A 1/3-scale "thin-slice" model of an electric arc furnaces was developed so that gas could be injected to simulate slag foaming. The influence of arc jets, oxygen lancing and bottom bubbling was also simulated. Liquid velocities were measured by a white light particle image velocimetry system. The results are compared with mathematical models.

11:10 AM

PHYSICAL AND MATHEMATICAL MODELLING INVOLVING EXOTHERMIC REACTIONS IN LIQUID METALS: *Stavros A. Argyropoulos*[1]; Hongfa Hu[2]; Stephan Ferenczy[3]; [1]University of Toronto, Dept. of Metall. and Mats. Sci., Walberg Bldg., Room 142, 184 College St., Toronto, Ontario M5S 3E4 Canada; [2]Meridian Magnesium North America, Strathroy, Ontario N7G 1H4 Canada; [3]FUCHS Systems, Inc., Salisbury, NC USA

Physical as well as mathematical modeling was carried out to investigate the exothermic mass transfer in liquid metals systems. In these systems, the heat, mass and momentum transfer is deeply coupled. Moreover, these deeply coupled systems are further complicated by the presence of a moving boundary. In the physical model used, ice cylinders were immersed into sulfuric acid solutions, because the intermixing of ice with sulfuric acid is very exothermic. In this low temperature system, velocity and temperature measurements in the sulfuric acid were made. In addition, measurements of ice melting in the sulfuric acid were carried out. The mathematical model developed solved the heat, mass and momentum equations numerically, utilizing the control-volume finite difference approach. The enthalpy method was adopted to track the moving boundary. Predictions made by the mathematical model were in close agreement with the results obtained by the physical model. The results from the mathematical model were further validated with high temperature liquid metals. Specifically, data were obtained in an experimental setup involving (a) dipping silicon cylinders into high carbon liquid iron and (b) dipping nickel cylinders into liquid aluminum. Results from these experimental studies supported the predictions that had been made using the mathematical model.

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MODEL STUDIES OF HEAT TRANSFER AND FLOW IN SLAG-CLEANING FURNACES: S. Kang[1]; *David Gordon Campbel Robertson*[1]; [1]University of Missouri Rolla, Dept. of Metall. Eng., 215 Fulton Hall, Rolla, MO 65409-1460 USA

Slag cleaning furnaces require extensive wall cooling because they involve the use of a superheated slag bath. This is in direct contrast to smelting furnaces, where the wall is usually (but not always) protected by "banks" of solid charge. In order to understand the heat transfer and flow in slag cleaning furnaces a number of model studies have been carried out using molten wax to simulate the slag. Wax is a good model fluid because, like slag, it has low Prandtl number. Wax models cannot simulate the behavior close to the electrodes (DC arc or AC submerged), but they can and do give a good simulation of the flow and heat transfer at the wall. An understanding of these phenomena is of great importance is the design of cooling panels in the walls of the furnace. Since superheated molten slag will eventually wear away any reasonably priced refractory bricks, the wall cooling must be designed to form a "freeze lining". The heat flux density (Q/A) required to do this is given by Q/A = h*(deltaT), where h is the heat transfer coefficient in the slag phase at the wall, and (deltaT) is the superheat (bulk slag temperature - liquidus

temperature). Both Q/A and h vary greatly with position and both are usually a maximum at the slag line. In the experimental work molten wax baths were heated by block heaters to provide similar energy densities (MW/m3) to those encountered in commercial slag cleaning furnaces. This procedure was considered to be valid since most of the electrical energy into a furnace bath is dissipated as heat. Gas stirring was used to simulate the gas evolved at the electrode in real furnaces - the quantity of this gas could be estimated from a knowledge of electrode consumption. The similarity criterion was equal gas flow per unit area of surface, in model and prototype. Heat transfer coefficients were measured in the models as a function of power density, gas stirring, superheat, etc., and could be related to the full scale operations by the use of dimensional analysis. The flows, heat transfer coefficients, etc., were also measured in a simple rectangular geometry and the flow was modeled using the COMPACT-2D software package. Good agreement was obtained between the experimental data and the model predictions.

FLUID-FLOW PHENOMENA IN METALS PROCESSING: Solidification and Casting: Computation and Experiments

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

Wednesday AM Room: 5B
March 3, 1999 Location: Convention Center

Session Chairs: Doru M. Stefanescu, The University of Alabama, Dept. of Metall. and Mats. Eng., Tuscaloosa, AL 35487-0202 USA; Robert A. Stoehr, University of Pittsburgh, Dept. of Mats. Sci. and Eng., Pittsburgh, PA 15261 USA

8:30 AM
FLUID FLOW PHENOMENA AND SOLIDIFICATION BEHAVIOR DURING THE CASTING OF A Pb-Sb-Sn ALLOY: *Matthew John M. Krane*[1]; [1]Purdue University, School of Materials Engineering, 1289 MSEE Bldg., West Lafayette, IN 47907 USA

Using a new numerical treatment of transport phenomena occurring during the solidification of ternary metal systems, the macrosegregation patterns and convective behavior of a Pb-5wt%Sb- 35wt%Sn alloy are studied. At this composition, the solidification which occurs while the local liquid composition is in the (Pb)-(SbSn) binary eutectic trough has a significant effect on these phenomena. The effects of this solidification path on fluid flow and macrosegregation are compared to the more familiar binary alloy patterns. The effects of solid particle transport and mushy zone permeability are also evaluated. The final predictions of macrosegregation are compared to measured composition profiles.

8:50 AM
GRAIN STRUCTURE EVOLUTION IN Al-Cu ALLOYS SOLIDIFYING DURING UNIDIRECTIONAL FLOW OVER A CHILL: COMPARISON OF A CA MODEL WITH EXPERIMENTS: *Robert A. Stoehr*[1]; Chidchai Loyprasert[1]; [1]University of Pittsburgh, Dept. of Mats. Sci. & Eng., 848 Benedum Hall, Pittsburgh, PA 15261 USA

A computer model has been developed to predict grain structure in alloys solidified under unidirectional flow using a combination of three techniques — solution of the equations for flow of an incompressible fluid bounded by curved surfaces by the SOLA-SURF algorithm, calculation of heat flow by a finite volume method, and simulation of grain formation by a two-dimensional cellular automaton (CA) model. The changing rigid surface has been taken into account. Heterogeneous and homogeneous nucleation are considered, and the growth kinetics of a dendrite tip are evaluated by the Kurz-Giovanola-Trived (KGT) model. These calculations were applied to solidification of an Al-4.5% Cu alloy flowing over a chill on the bottom of a channel, a system for which experimental results were available. Using a variety of flow rates and superheats, agreement between the computed and experimental results were very good including transitions between columnar and quasi-equiaxed grains, the aspect ratio of the grains, and the inclination of the grains to the flow.

9:10 AM
AN EXPERIMENTAL STUDY OF THE SOLIDIFICATION OF PURE SUCCINONITRILE AND A SUCCINONITRILE-ACETONE ALLOY: James E. Simpson[1]; Henry C. de Groh[2]; Mark McDowell[2]; *Suresh V. Garimella*[1]; [1]University of Wisconsin - Milwaukee, Mech. Eng. Dept., P.O. Box 784, Milwaukee, WI 53201 USA; [2]NASA Lewis Research Center, MS 105-1, Cleveland, OH 44135 USA

An experimental study of the horizontal Bridgman growth of pure succinonitrile (SCN) and of a succinonitrile-1.0 mol.% acetone alloy (SCN-1.0 mol.% ACE) has been performed. Experiments involving both a stationary thermal field (no-growth case) and a translating thermal field (growth case) were conducted. Growth rates of 40 and 2 micro-m/s were investigated. For the pure SCN experiments, the velocity field in the melt was measured using Stereo Imaging Velocimetry (SIV). Measurements indicate that a primary longitudinal convective cell is formed. The maximum magnitude of the convective velocity in the pure case was 1.6 mm/s for both no-growth and steady growth. The shape of the solid/liquid interface was also quantitatively determined. The solid/liquid interface was stable (non-dendritic and non-cellular); however, it was not flat. Rather, it was significantly distorted by the influence of convection in the melt and, for the growth case, by the moving temperature boundary conditions along the ampoule. It was found that the interface shape and position were highly dependent on the alignment of the ampoule in the apparatus. Consequently, the ampoule was carefully aligned for all experiments. The values for front location agree with those determined in previous experiments. For the alloy experiments, the solid/liquid interface was determined to be unstable at growth rates of greater than 2.8 micro-m/s, but stable for the no-growth and growth at 2 micro-m/s cases. When compared to the shape of the pure SCN interface, the alloy interface forms closer to the cold zone, indicating that the melting temperature has been suppressed by the addition of the alloying element. Temperature measurements were taken at various locations on the outside of the ampoule, in order to determine the thermal boundary condition on the ampoule. The resulting thermal profiles are presented in detail. It is intended that the interface shape, thermal boundary condition and velocity field data presented in this paper be used to test numerical simulations.

9:30 AM
CONVECTION INDUCED PATTERN FORMATION IN DIRECTIONAL SOLIDIFICATION: *Prantik Mazumder*[2]; Rohit M.I.K. Trivedi[1]; [1]Ames Laboratory, US-DOE, Dept. of Mat. Sci. and Eng., Ames, IA 50011 USA; [2]Iowa State University, Dept. of Mech. Eng., Ames, IA 50011 USA

Numerical analysis is carried out to examine the effects of thermosolutal convection on formation of patterns in directionally solidified binary alloys. A finite-difference analysis is used for dynamic modeling of a prototype Vertical Bridgman system that takes into account heat transfer in the melt, crystal, and the ampoule; melt flow and solute transport. Actual temperature data from experimental measurement are used for accurately describing the thermal boundary conditions. The convection is found to consist of two vertically stacked torroidal cells. The flow in the upper cell is upwards along the ampoule wall and is driven by the large radial temperature gradient at the junction of the hot zone and the adiabatic zone. The cell adjacent to the solid

liquid interface has complex dynamics depending on the location of the interface relative to the furnace configuration, thermal conductivities of crystal, melt and the ampoule, and the thermal and solutal Rayleigh numbers. The flow range from minimal convection to steady cellular and multi-cellular convection to periodic convection to quasiperiodic to intense turbulent mixing. The convection in binary alloys with destabilizing solutal effect on convection (for which the rejected solute is lighter than the solvent, e.g. Pb-Sn and Pb-Bi) usually undergoes rapid transition to intense turbulent convection from steady cellular/multicellular convection. In alloys with stabilizing solutal effect (the rejected solute is heavier than the solvent, e.g. Al-Cu and Sn-Cd) the convection evolves through a distinct set of bifurcations and the intensity of mixing is relatively smaller. For peritectic alloys (Sn-Cd, Pb-Bi) a two phase oscillating microstructure may develop in response to the oscillating segregation profile. For single phase alloys a large lateral disorder in cell spacing may occur in low convective systems (Al-Cu) compared to high convective system (Pb-Bi). The numerical calculations are found to agree well with experiments done with the systems mentioned.

9:50 AM

SINGLE AND MULTIPHASE FLOWS GENERATED BY ROTATING ELECTROMAGNETIC FIELDS: APPLICATION TO THE CRYSTALLIZATION OF THIXOTROPIC ALUMINUM ALLOYS SLURRIES AND COMPOSITES: *Charles Noël Vivés*[1]; [1]Université d'Avignon, Laboratoire de Magnétohydridynamique, 33, Rue Pasteur, Idem, Avignon, Vaucluse F84000 France

The elaboration of thixotropic alloys slurries and metal matrix composites requires a very vigorous stirring, often produced by rotating electromagnetic fields. In the case of relatively small section ingots of light metals (aluminum or magnesium alloys), the free surface deepness can reach several meters, and becomes then unacceptable. Indeed, a deep vortex is responsible for an undesirable entrapment of gas and oxides into the bulk of the melt during the mixing and solidification processes. This circumstance leads to porosity in casting and, in the case of composites, inhibits wetting at the slurry-particle interface to the detriment of bonding properties. The main goal of this experimental work was to overcome these specific and serious drawbacks through the use of two three-phase motor stators able to produce either single or contra-rotating flows. In this investigation, the working fluids were mercury and aluminum alloys. The approach was to measure separately the electromagnetic parameters, namely the magnetic field and current density components as well as the phase angle between these periodic vectors, and next to obtain the electromagnetic force field from these parts. Then, these results were connected with the experimentally determined free surface shape, velocity field and turbulence. Satisfactory results concerning the microstructure of solidified aluminum alloys slurries and aluminum alloy matrix composites (homogeneity, crystal shape, grain size, fraction of primary solid, and distribution of SiC particles) were obtained.

10:10 AM BREAK

10:30 AM

A PIV-BASED PHYSICAL MODEL FOR OSCILLATING GRAVITY INDUCED CONVECTION: M. Higgins[1]; B. R. Ramaprian[1]; *Ben Q. Li*[1]; [1]Washington State University, School of Mechanical and Materials Engineering, Pullman, WA 99163 USA

In designing metals processing systems for space applications, oscillation convective flows induced by transient g-jitter or residual gravity field must be considered. This paper presents a ground based experimental study of oscillating convection, with an intention to simulate some of basic g-jitter effects. Towards this end, a physical model is developed. The model uses water as working fluid and oscillating wall temperature is applied The oscillating convective flows in the model are visualized using a laser-based PIV system. With the model, various parameters affecting flows can be studied. Measured results for convective flows will be presented and compared with those obtained from a finite element model.

10:50 AM

GRAVITATION EFFECTS ON MACROSEGREGATION - EXPERIMENTS AND COMPUTATIONAL MODELING: *Jose Leon-Torres*[1]; Doru M. Stefanescu[1]; Subhayu Sen[2]; Peter A. Curreri[3]; [1]University of Alabama, Solidification Laboratory, College of Engineering, P.O. Box 870202, Tuscaloosa, AL 35487 USA; [2]USRA, NASA Marshall Space Flight Center, ES75, Huntsville, AL 35812 USA; [3]NASA Marshall Space Flight Center, ES75, Huntsville, AL 35812 USA

Experiments were performed under terrestrial gravity (1g) and during parabolic flights (10-2 g) to study the solidification and macrosegregation patterns of Al-Cu alloys. Alloys having 2% and 5% Cu were solidified against a chill at two different cooling rates. Microscopic and Electron Microprobe characterization was used to produce microstructural and macrosegregation maps. In all cases positive segregation occurred next to the chill because shrinkage flow, as expected. This positive segregation was higher in the low-g samples, apparently because of the higher heat transfer coefficient. A 2-D computational model was used to explain the experimental results. The continuum formulation was employed to describe the macroscopic transports of mass, energy, and momentum, associated with the solidification phenomena, for a two-phase system. The model considers that liquid flow is driven by thermal and solutal buoyancy, and by solidification shrinkage. The solidification event was divided into two stages. In the first one, the liquid containing freely moving equiaxed grains was described through the relative viscosity concept. In the second stage, when a fixed dendritic network was formed after dendritic coherency, the mushy zone was treated as a porous medium. The macrosegregation maps and the cooling curves obtained during experiments were used for validation of the solidification and segregation model. The model can explain the solidification and macrosegregation patterns and the differences between low- and high-gravity results.

11:10 AM

VISUALIZATION OF DYNAMIC BEHAVIOR OF IMMISCIBLE LIQUIDS DURING SOLIDIFICATION OF MONOTECTIC SYSTEMS: *J. B. Andrews*[1]; L. J. Hayes[1]; L. J. Little[1]; [1]University of Alabama at Birmingham, Dept. of Mats. and Mech. Eng., 1150 10th Ave. S., BEC 254, Birmingham, AL 35294 USA

This presentation will cover results obtained from the microgravity glovebox investigation Wetting Characteristics of Immiscibles, which flew aboard the space shuttle Columbia during the USMP-4 flight in November and December of 1997. In this investigation, twelve compositions within the transparent succinonitrile-glycerine immiscible system were studied. The main intent of the investigation was to directly observe the events which lead to gross phase separation during microgravity processing of many immiscible alloys. One theory proposes this separation occurs when one of the immiscible liquid phases perfectly wets the walls of the container in which the alloys are processed. The wetting characteristics were varied in this investigation by varying the sample compositions. Perfect wetting of the container walls by the minor liquid phase was observed in several cases. In addition, flow was observed in some of the sample cells which appeared to be associated with the coalescence of droplets. This flow was particularly interesting in cases where the two immiscible liquids were present in roughly equal proportions. Video demonstrating the wetting behavior and the flows observed during this microgravity glovebox investigation will be shown as part of this presentation.

11:30 AM

THE EFFECT OF FLUID FLOW ON A SEDIMENTING PARTICLE NEAR A SOLIDIFYING INTERFACE: *Anthony Michael John Davis*[1]; [1]University of Alabama, Dept. of Math., 345 Gordon Palmer Hall, P.O. Box 870350, Tuscaloosa, AL 35487-0350 USA

The doping of binary substances with a small volume fraction of second phase inclusions is used in the solidification processing of MMC's to improve the material properties of the final cast. The presence in the melt of a solid particle of different conductivity causes modification to the temperature and solute concentration fields which together displace the interface through distances assumed here to be small enough for linearization. The determination of the interface profile from the compatibility condition is somewhat complicated. The interface displacement also contributes to the fluid flow in the melt and, in particular, to the velocity of sedimantation of the particle.

GENERAL ABSTRACTS: Session 7 - Issues in Materials Science: Thin Films & Temperature Sensing

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

Wednesday AM Room: 12
March 3, 1999 Location: Convention Center

Session Chairs: Dr. Mark Palmer, Virginia Commonwealth University, Dept. of Mech. Eng., Richmond, VA 23284-3015 USA; Elliot Schwartz, The Gillette Company, South Boston, MA 02127-1096 USA

8:30 AM

A NOVEL TECHNIQUE FOR NON-CONTACT TEMPERATURE MEASUREMENT OF SEMICONDUCTOR WAFERS: *Assaf Thon*[1]; Evgeny D. Glazman[1]; [1]3T, Theradion Industrial Park, Misgav 20179 Israel

Single wafer equipment semiconductor manufacturing performs a variety of thermal deposition and annealing processes. The operating temperature range is typically between 350°C to 1200°C and the pressure varies between 10-5 Torr to near atmospheric pressure. A firm window of working parameters characterizing every specific process should be maintained within a pre-set and usually small tolerance. While much effort is invested in widening the window of parameters, it is still necessary to keep the temperature error as small as some fractions of a percent of the set point. The trends towards smaller device dimensions (0.25 micron and below) and bigger wafer size (300 mm) impose clear standards on the equipment performance metrics. In this work we represent results of a novel technique for precise and accurate measurement of semiconductor wafers temperature. The technique combines multispectral passive and active methods. The true emissivity of the wafer is calculated dynamically at high rat. An accuracy of better than 1% was demonstrated for Si wafers with varied emissivity between 0.2 to 0.9, at the temperature range of 400°C to 850°C. Current work is now being done on increasing the accuracy to better than 0.5% for all emissivity range and up to 1200°C.

8:55 AM

CARBON FIBER EPOXY-MATRIX COMPOSITE FOR TEMPERATURE SENSING: Shuokai Wang[1]; *Deborah D. L. Chung*[1]; [1]State University of New York at Buffalo, Mechanical and Aerospace Engineering, 608 Furnas Hall, Amherst, NY 14260 USA

A polymer (epoxy)-matrix composite with the top two laminae of continuous carbon fibers in a crossply configuration was found to be a temperature sensor. Each junction between crossply fiber tow groups of adjacent laminae is a sensor, while the fiber groups serve as electrical leads. A junction array provided by two crossply laminae allows sensing of the temperature distribution. The contact electrical resistivity of a junction decreases reversibly upon heating (whether using light or hot plate to heat), due to the activation energy involved in the jump of electron across the junction. The contact resistivity decreases with increasing pressure during composite fabrication, due to the increase in pressure exerted by fibers of one lamina on those to the other lamina. The absolute value of the fractional change in contact resistivity per degree C increases with increasing pressure during composite fabrication, due to decrease in composite thickness, increase in fiber volume fraction and consequent increases in interlaminar stress and activation energy. A junction between unidirectional fiber tow groups of adjacent laminae is much less effective for temperature sensing, due to the absence of interlaminar stress.

9:20 AM

THERMODYNAMIC STABILITY OF SELECTED TERNARY COMPOUNDS IN THE Cu-In-Se SYSTEM BY A SOLID ELECTROLYTE EMF TECHNIQUE: *Pankajavalli Nagarajan*[1]; Muhsin Ider[1]; Chih-hung Chang[1]; Timothy J. Anderson[1]; [1]University of Florida, Dept. of Chemical Engineering, P.O. Box 116005, Gainesville, FL 32611 USA

Polycrystalline thin films of $CuInSe_2$ are a promising material for high efficiency photovoltaic solar cells in low-cost power generation applications. The four ternary compounds $CuInSe_2$, $Cu_2In_4Se_7$, $CuIn_3Se_5$ and $CuIn_5Se_8$ were reported to be contained in the Cu_2Se-In_2Se_3 pseudobinary system and can be important in the synthesis of high efficiency cells. The phase equilibria and thermochemistry of the Cu-In-Se system, however, is not well established. In particular, ambiguity exists about the location of the phase boundary between the chalcopyrite(α) and sphalerite(δ) phases of $CuInSe_2$. In addition, no thermodynamic data are available on the stability of these ternary phases, except the standard entropy and enthalpy of formation of $CuInSe_2$. The EMF of the following galvanic cells were measured: $W|In(l),In_2O_3(s)||YSZ||In_2O_3(s)$, $Cu_2Se(s)$, $Cu(s)$, $CuInSe_2(\alpha$ or $\delta)|C|W$ (I) $W|In(l),In_2O_3(s)||YSZ||In_2O_3(s)$, $Cu_2In_4Se_7(s)$, $CuInSe_2(\alpha$ or $\delta)$, InSe(s or l)$|C|W$ (II) $W|In(l),In_2O_3(s)||YSZ||In_2O_3(s)$, $CuIn_5Se_8(s)$, $CuIn_3Se_5(s)$, InSe(l)$|C|W$ (III). Measurements on the three cells were made using a 15 mol% yttria stabilized zirconia solid electrolyte in the temperature ranges 949 to 1150, 868 to 1179 and 977 to 1145K respectively. Combining literature data for the standard Gibbs energies of formation of Cu_2Se, InSe and $CuIn_3Se_5$ with the standard Gibbs energy changes determined from the above cells, the standard Gibbs energy of formation of $CuInSe_2$, $Cu_2In_4Se_7$ and $CuIn_5Se_8$ were determined to be $\Delta G°f\ CuInSe_2\ (\alpha) \pm 0.51$ (kJ mol^{-1}) = - 35.60 - 0.1718 T(K) $\Delta G°f\ CuInSe_2\ (\delta) \pm 0.18$ (kJ mol^{-1}) = - 13.91 - 0.19296 T(K) $\Delta G°f\ Cu_2In_4Se_7(s) \pm 1.94$ (kJ mol^{-1}) = - 596.88 - 0.04972 T(K) $\Delta G°f\ CuIn_5Se_8(s) \pm 1.97$ (kJ mol^{-1}) = - 1086.56 + 0.31051 T(K). From the above results, the α to δ phase transition temperature and the enthalpy of transition for $CuInSe_2$ were determined to be 1025K (from cell I), 1050K (from cell II) and 21.7 kJ mol^{-1} respectively. These results have been included in an optimization of the Cu_2Se-In_2Se_3 pseudobinary phase diagram. The implications for processing $CuInSe_2$ solar cells will be discussed.

9:45 AM

THE METALLURGY OF ARTIFICIAL DIAMOND FILM PLANARIZATION: *Khershed P. Cooper*[1]; James E. Butler[2]; [1]Naval Research Laboratory, Materials Science & Technology, Code 6321, 4555 Overlook Ave., SW, Washington, D.C. 20375-5343 USA; [2]Naval Research Laboratory, Chemistry Division, Code 6174, 4555 Overlook Ave., SW, Washington, D.C. 20375 USA

Potential applications of artificial diamond films are in cutting tools, thermal management, electronic devices and optical windows. To be functional, the rough faceted growth surface of the diamond film has to be planarized. One method of accomplishing this is thermochemical planarization. In our experiments, we held the diamond film in intimate contact with a flat piece of iron at a temperature below the Fe-C eutectic. As carbon atoms from the diamond diffused into the iron, the growth facets were removed and planarization occurred. We studied the effect of applied load, hold time and temperature on the planarization process. While the effect of load was linear, the influence of time and temperature appeared parabolic. Examination of the diamond/iron interface showed that as carbon diffusion proceeded, thin graphite and cementite films formed between the diamond and the iron. After planarization, the diamond film retained its structure, but the dissolution of carbon into the iron resulted in transformation products such as very finely spaced pearlite. The presence of cementite along the grain boundaries deep into the iron piece showed that carbon diffused to a greater length along grain boundaries. But due to the coarsened grain structure, the grain boundaries were too few to accelerate the diffusion process. Quantification of the faceted growth surface and estimations of the diffusion rates in Fe-C alloys helped understand the process kinetics.

10:10 AM
DEVELOPMENT OF ROUGHNESS IN ULTRATHIN ELECTRODEPOSITED TRILAYER FILMS: Rob Renner[1]; Bo Dou[1]; *Knona Liddell*[1]; [1]Washington State University, Chemical Engineering Dept., P.O. Box 642710, Pullman, WA 99164-2710 USA

Layered Co/Cu/Co and Ni/Cu/Ni films were electrodeposited onto a vapor deposited Cu seed layer on Si using the stepped potential, single bath technique and an unstirred aqueous electrolyte. In separate experiments, the thickness of each layer was varied between 2 and 20 nm. Atomic force microscopy was used to measure both the RMS peak height and the areal peak density; the substrate, single Co or Ni layers, and bi- and tri-layer samples were examined. The Co-Cu and Ni-Cu systems show qualitatively similar behavior. Increased peak height is linearly correlated with decreased peak density for the thinnest films, but neither height nor density is directly related to film thickness.

10:35 AM
MODELING ORIENTED NUCLEATION AND GRAIN GROWTH IN COPPER ELECTROCOATINGS: *O. B. Girin*[1]; [1]State Metallurgical Academy of Ukraine, Dept. of Physics, Prospekt Gagarina 4, Dnipropetrovak 32063 Ukraine

A thermodynamic and a mathematical model of texture formation in copper electrocoatings is discussed. The respective contributions of the grain boundary energy, the surface energy and the bulk energy to the driving force of texture formation in the coatings at the nucleation stage and using the grain growth of the major component are addressed. Estimates of shape anisotropy are given for texture nuclei and oriented grains in relation to anisotropy of electrocoating properties. Optimum process conditions are cited that allow the most developed texture and the most desired properties of copper electrocoatings.

11:00 AM
SOME ENGINEERING APPLICATIONS OF MATERIALS SCIENCE; SENSORS FOR HYDROGEN OR OXYGEN: David R. Morris, Dept. of Chemical Engineering, University of New Brunswick, Fredericton, NB E3B 5A3 Canada

This paper describes the exploitation of the properties of two materials for the development of chemical sensors: 1. The per fluorinated ionomer, Nafion H is a hydrogen ion conductor. This material property is utilized for the construction of a solid state electrochemical sensor for monitoring hydrogen in pipeline steel and for monitoring hydrogen or oxygen in high temperature water. The uptake of hydrogen into the pipeline steel at ambient temperature is strongly promoted by the presence of hydrogen sulphide. The sensor for application too high temperature (to ~500 K) water is a non-isothermal electrochemical cell with the reference electrode (Fe^{II}, Fe^{III} sulphate hydrates) at ambient temperature. Nafion is in the form of small diameter tube. The sensor voltage is a function of the dissolved hydrogen (or oxygen) concentration in the water and a function of the temperature at the sensing electrode. 2. The electrical resistance of palladium at a fixed temperature is a function of the concentration of hydrogen. This material property is utilized for the construction of a sensor for monitoring hydrogen (or deuterium) in high temperature (to ~570 K) water. Measurements of the electrical resistance of a palladium wire in hydrogen/inert gas mixtures and in hydrogen/water solutions permit determination of the Henry Law constant for hydrogen in water. Values of the Henry Law constant so determined are lower than values published in the literature, which were determined by equilibrium experiments.

GENERAL RECYCLING OF MATERIALS: Recycling of Aluminum and other Light Metals

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 Metallic Materials, Berlin D-10623 Germany

Wednesday AM Room: 1A
March 3, 1999 Location: Convention Center

Session Chairs: Gerrit H. Nijhof, Hoogovens , R & D, IJmuiden The Netherlands; Ray D. Peterson, IMCO Recycling, Irving , TX 75039 USA; Benji Maruyama, US Air Force, Research Lab., Wright Petterson AFB, OH 45433 USA

8:30 AM OPENING REMARKS

8:35 AM INVITED PAPER
UPGRADING OF NON-FERROUS METAL SCRAP, PARTICULARLY ALUMINIUM, FOR RECYCLING PURPOSES.: *Gerrit Nijhof*[1]; [1]Nijhof Consultancy, Heemsteedse Dreef 92, 2102 KN Heemstede The Netherlands

After the consumer phase of most products it is often difficult to separate the different metals present, particularly non-ferrous metals and stainless steels. A mixing of metal scrap will occur. When this mixture is directly melted a metal is produced with high amounts of impurities. These metals are suitable for application as casting alloys only. To prevent the mixing of scrap, separation at the source is required. Recently several techniques for separation of non-ferrous metals have become available. The following techniques will be discussed: 1. Eddy Current separation; to separate non-ferrous metals from a mixture of waste; 2. Fluid bed separation; to separate light and heavy metals; 3. Separation by image analysis; to separate cast and wrought alloys. Results of different recent experiments, using these techniques will be presented. However, when a separation of scrap is not possible a removal of undesired elements must be performed. Techniques, developed on laboratory scale have been presented at previous Light Metals Conferences and will be shortly reviewed.

9:00 AM
A SMALL-SCALE RECYCLING PROCESS FOR NON-FERROUS ALLOYS: *Richard Johnson*[1]; [1]TWI, Electron Beam, Friction & Forge Processes Dept., Abington Hall, Abington, Cambridge CB2 6AL UK

Large firms can invest in furnaces to recycle aluminium alloy scrap back into the production process, but smaller firms are less able to do so on economic grounds. They therefore obtain very low returns on their scrap arisings, as they are essentially paying for the transport of air and only some metal to the recyclers. Friction extrusion is one of a stable of friction technologies developed by TWI, which consolidates scrap directly into solid product. By generating the necessary heating locally by friction, the energy consumption of the process is very low, whilst the consolidation of the material is effected in the solid phase rather than by melting. This means there are minimal material losses from oxidation, and little fume generation when dealing with scrap contaminated by machining fluids, etc. The paper will review the process limitations and advantages, including the environmental benefits, and its applicability to a range of aluminium alloys and other non-ferrous materials.

9:25 AM
COLOR SORTING ALUMINUM ALLOY SCRAP FOR RECYCLING: *Rebecca K. Wyss*[1]; Paul B. Schultz[1]; [1]ALCOA, Technical Center, 100 Technical Dr., Alcoa Center, PA 15069-0001 USA

The ability to recycle and reuse scrapped materials increases in importance as the use of aluminum alloys in automotive and other applications continue to expand. Color sorting is a new process which has the capability to sort mixed alloy scrap so that it can be recycled into new wrought alloys. Aluminum manufacturers can use sorted scrap to make wrought alloys and replace high cost primary metal, currently used to produce wrought alloys, with lower cost metal units. Ultimately, the energy savings and economic and environmental benefits would be significant, substantially increasing the value of aluminum. The color sorting process involves chemically etching similar appearing scrap to color the scrap according to its chemical composition. The color differences are sufficient to allow optical recognition systems to automatically identify and separate scrap by alloy family for recycling. The distinct appearance of alloys from each of the 2xxx, 3xxx, 5xxx, 6xxx, and 7xxx alloy groups, which have been etched using commercially acceptable chemical treatments, will be presented.

9:50 AM BREAK

10:05 AM
DECOATING OF ALUMINIUM PRODUCTS AND THE ENVIRONMENT: *Richard Joseph Evans*[1]; Graham Guest[1]; Willis Bateman[1]; [1]Stein Atkinson Stordy, Ltd., Aluminium Division, Midland House, Ounsdale Rd., Wombourne, Wolverhampton WV5 8BY UK

This paper focuses on the environmental aspects of decoating aluminium products. Over the past ten years, Stein Atkinson Stordy have built up a considerable knowledge of the decoating process and its environmental criteria. The basic environmental standards applicable to decoating are outlined for both the European and American markets and their major differences highlighted. Types of scrap and their associated coating are discussed, together with typical emissions encountered and suitable methods of their environmental control. Aspects of plant design and operation, with typical field results are presented to reinforce the theoretical aspects of the body of the paper.

10:30 AM
BATH RECOVERY FROM CARBON DUST BY FROTH FLOTATION: *Juan J. del Campo*[1]; Mario Menéndez[2]; Juan M. Menéndez[2]; [1]Universidad de Oviedo, Dept. of Mats. Sci. and Eng. Metall., Avda. Manuel Llaneza 75, Gijon, Principado de Asturias 33208 Spain; [2]Universidad de Oviedo, Mining, Exploration and Operation, Escuela de Minas de Oviedo, Independencia 13, Oviedo, Principado de Asturias 33004 Spain

Carbon dust produced in the operation of aluminum electrolysis pots is a hazardous waste. It contains valuable fluorides and coke. There is a potential interest in the separation of both fractions in order to returnthe cryolite bath into the pots. A froth flotation process is proposed. The degree of liberation of carbon together with the operating conditions of the flotation plant are studied. Industrial experience at INESPAL METAL,S.A. with recycled bath is also presented.

10:55 AM INVITED PAPER
IMPROVING EFFICIENCY AND EMISSION REDUCTION - SOURCE PROCEDURES IN SECONDARY ALUMINUM INDUSTRY: *Ina Ollenschlaeger*[1]; [1]VAW Aluminium AG, Forschung und Entwicklung, Entwicklungszentrum Recycling, Georg-von-Boeselager-Str. 25, Bonn D-53117 Germany

Aluminum is used in many different products: from thin foil in packaging material over automotive components up to building applications. The various scraps of these products and their wide range of non-metallic components like paper, lacquers, and oils may cause a high level of emissions, especially dioxins. To avoid this output into the atmosphere, secondary processes like waste gas purification techniques are required which generate themselves contaminated materials and in any case cost. Another way to reduce emissions as dioxins and others and minimize energy input is by regulating source procedures like (in case of rotary drum furnace) variations in burner and charging technology, waste gas guidance, and process parameters. The experiments have been carried out in the recycling center, which is part of VAW Aluminium AG, department for research and development. As test equipment a rotary furnace in pilot scale (500 kg) was used and the emission, energy and mass balance were determined.

11:20 AM CLOSING REMARKS

HIGH TEMPERATURE COATINGS III: Ceramic and Intermetallic Coatings

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

Wednesday AM Room: 19
March 3, 1999 Location: Convention Center

Session Chairs: Michael J. McNallon, University of Illinois at Chicago, CME Dept., Chicago, IL 60607 USA; Robert J. Hanrahan, Los Alamos National Laboratory, Mats. Sci. and Tech. Div., Los Alamos, NM 87545 USA; Janet M. Hampikian, Georgia Institute of Technology, Dept. of Mats. Sci. and Eng., Atlanta, GA 30332-0245 USA

8:30 AM
THE EFFECT OF REACTIVE ELEMENT ADDITIONS ON THE OXIDATION OF BERYLLIUM MODIFIED NiAl: *R. J. Hanrahan*[1]; D. J. Thoma[1]; [1]Los Alamos National Laboratory, Mats. Sci. & Tech. Division, MST-6, TA 3 MS G770, Los Alamos, NM 87545 USA

Be may be solutionally substituted for Al in NiAl at up to 5-7 a/o. In our previous studies we have determined that at levels as low as 1 a/o Be that a protective oxide layer formed which consists of the spinel $BeAl_2O_4$. The usual transient alumina phases have never been observed to form under any exposure conditions tested. The oxide is extremely smooth and adherent however we still observe void formation at the metal-oxide interface and under cyclic oxidation or exposure above 1100°C the scale spalls in a manner similar to binary NiAl. We have therefore added several different reactive elements (Y, Zr, various lanthanides) to arc-cast ingots of Ni-48Al-2Be to determine whether these additions might further improve the oxide stability relative to the ternary alloy. Cyclic and static oxidation tests were conducted at 1000 and 1200°C in moist air.

8:50 AM
DEVELOPMENT OF HIGH TEMPERATURE SULFIDATION RESISTANT Fe-Al WELD OVERLAY COATINGS: *S. W. Banovic*[1]; J. N. DuPont[1]; P. F. Tortorelli[2]; A. R. Marder[1]; [1]Lehigh University, Whitaker Lab, 5 East Packer Ave., Bethlehem, PA 18015 USA; [2]Oak Ridge National Laboratory, Oak Ridge, TN 37831 USA

Fe-Al alloys, with low aluminum contents, are being investigated for use as corrosion protective weld overlay coatings. Previous research has demonstrated that compositions in the intermetallic regime have excellent high temperature sulfidation resistance. However, their low strength at high temperatures and lack of weldability limit their usage. Therefore, research has been initiated to study compositions in the disordered region which have lower amounts of aluminum. The high temperature sulfidation behavior of alloys with aluminum contents of 5-12.5 wt% Al was investigated using thermogravimetric techniques. These compositions are located near the crack/no crack boundary previously found during weldability studies. Samples were isothermally held in a reducing

gas (H_2-H_2S-Ar) at temperatures ranging from 500-700ϒC. Light optical and scanning electron microscopy were used to analyze the corrosion scales. Compositions of these reaction products were determined using electron probe microanalysis (EPMA). Depending upon the temperature, composition of the gas, and aluminum content of the alloy, various surface scales were observed to form. Those that developed an aluminum oxide scale were relatively protective and had very low weight gain. Samples that formed iron sulfide scales were generally less protective than those previously mentioned, but had lower weight gains than carbon steel and 309 stainless steel. These results indicate good promise for the practical application of Fe-Al overlay coatings in reducing environments.

9:10 AM

THE DEPOSITION OF CHROMIA, CHROMIA/YTTRIA, AND SILICA COATINGS VIA COMBUSTION CVD: Amanda E. Alexiou[1]; *Janet M. Hampikian*[1]; [1]Georgia Institute of Technology, School of Mats. Sci. and Eng., Bunger Henry Bldg., 778 Atlantic Dr., Atlanta, GA 30332-0245 USA

Combustion chemical vapor deposition was utilized to deposit chromia, 2 wt.percent yttria/chromia, and silica thin films onto Ni-20Cr. Amorphous phases of all three films were produced, as well as crystalline phases of both the chromia and chromia/yttria films. The phase generated depended on deposition temperature, which was varied between 220, for amorphous phase, and 500ϒC, for crystalline phase in the chromia films and from 700 to 800ϒC for the amorphous silica films. The films were characterized using SEM, TEM, EDS, and x-ray diffraction spectroscopy. The ability of the films to provide oxidation protection at 800ϒC was quantified using thermogravimetric analysis (TGA). All three types of coatings were deposited for 30 minutes and, in addition, the chromia films were also deposited for 15 and 7.5 minutes. The effects of film type and thickness were compared in the oxidation studies. All coatings reduced the oxidation kinetics of Ni-20Cr.

9:30 AM

NUMERICAL SIMULATIONS OF HVOF JET/SUBSTRATE INTERACTION: *S. Eidelman*[1]; X. Yang[1]; [1]Science Applications International Corporation, 1710 Goodridge Dr., McLean, VA 22102 USA

HVOF coatings of micro and nanoscale materials can present a problem when significant particle deceleration can occur in the stagnation region of jet/substrate interaction. Thus, very small particle will slow down and be diverted by the flow in the stagnation region. The material cannot be coated if it is composed of unagglomerated nanosized particles, because nanosize particles closely follow the streamlines of the carrying gas. This will result in powder loss and reduced coating efficiency and quality. We use comprehensive numerical simulation to examine the possible regimes for the coatings deposition considering the full range of system parameters for the HVOF jet/substrate interaction. We also explore the effect of nano-agglomerates density, size, and shape on coating efficiency, which can suggest the goals for materials preprocessing optimization. Rapid analysis of the parametric space using numerical simulations will shorten the time scale for new coating development and allow better understanding of the parameters that control coating efficiency and quality.

9:50 AM

HARDENING AND MICROSTRUCTURE OF ALUMINUM METAL SURFACE BY COMPLEX ALLOYING: *M. Okutomi*[1]; A. Obara[1]; K. Tsukamoto[1]; [1]Electrotechnical Laboratory, Opto-electronic Division, 1-1-4 Umeono, Tsukuba, Ibaraki 305 Japan

Hardening and microstructure of aluminum metal surface with CO_2 laser alloying assisted ultrasonic wave vibration technique have been investigated. A mixture of Al and Ti powder in an organic flux was painted onto the metal substrate followed by laser irradiation. To achieve uniform fine dendritic structure and to eliminate pores within the alloyed layer, laser irradiation was supplemented with ultrasonic vibration. Evaluation of the microstructure, hardness and tribological properties of the alloyed surface have been conducted. The alloyed surface consisted of dendrite structures of Ti_3Al and Ti-Al solid solution. The Ti_3Al dendrite appear to adhere effectively to other aluminum based phases thereby providing hardnesses for the alloyed surface in excess of 600 kg/mm^2. In addition, the wear resistance of the alloyed surface was about 1/7 time than that of the bare aluminum surface.

10:10 AM BREAK

10:25 AM

REACTION FORMED COATINGS FOR SiC FIBERS IN CERAMIC MATRIX COMPOSITES: *Michael J. McNallan*[1]; Daniel Ersoy[1]; Yury Gogotsi[2]; [1]University of Illinois at Chicago, CME Dept., M/C 246, Rm 3083 ERF, 842 W. Taylor St., Chicago, IL 60607 USA; [2]University of Illinois at Chicago, Mechanical Engineering, M/C 251, 842 W. Taylor St., Chicago, IL 60607 USA

A layer of compliant material is usually deposited on fibers for ceramic matrix composites to permit toughening by fiber pull out during failure. Chemical vapor deposition or sol gel techniques have usually been used to produce these coatings. These processes are expensive and sometimes fail to produce uniform, coherent coatings. Carbon films can be formed on SiC by selective chlorination of the silicon at high temperature and atmospheric pressure. The process is low cost and amenable to most SiC based fibers and whiskers. These films are generally of graphitic structure and can be further reacted to produce other coatings with better oxidation resistance.

10:45 AM

DEVELOPMENT OF A DIFFUSION BARRIER LAYER FOR HIGH-TEMPERATURE MOLYBDENUM ELECTRODES: *C. Suryanarayana*[1]; D. A. Buell[2]; D. Williamson[2]; J. J. Moore[1]; J. Disam[3]; [1]Colorado School of Mines, Advanced Coatings and Surface Engineering, Metall. and Mats. Eng., Golden, CO 80401-1887 USA; [2]Colorado School of Mines, Dept. of Physics, Golden, CO 80401 USA; [3]Schott Glaswerke, Mainz D-55014 Germany

Molybdenum electrodes are used in glass melting furnaces. To improve their oxidation resistance, especially at high temperatures, and also to match the coefficient of thermal expansion of molybdenum, application of a thin coating of a functionally graded $MoSi_2$+SiC layer is suggested. But, the problem with this coating is that silicon and carbon from the coating diffuse into the molybdenum substrate forming carbides and subsilicides resulting in the degradation and consequently losing the effectiveness of the coating. A diffusion barrier coating layer is being developed to overcome this problem. Reactive sputtering of an $MoSi_2$+1.96 mol SiC target in a nitrogen atmosphere produced an amorphous Mo-Si-C-N layer. This layer has been characterized for its structure and chemistry by a combination of techniques such as X-ray diffraction, differential thermal analysis, scanning electron microscopy, X-ray photon electron spectroscopy, and Auger electron spectroscopy. Annealing of this amorphous film at different temperatures was conducted to study the thermal stability of the amorphous layer and also to study its crystallization behavior. The results obtained on the microstructure, chemistry and the thermal stability of the diffusion barrier layer will be presented.

11:05 AM

PROTECTION OF HEATSTRESSED HYPERSONIC AIRCRAFT STRUCTURES MADE OF REFRACTORY MATERIALS BY NOVEL OXIDATION RESISTANT COATINGS: *V. Terentieva*[1]; [1]Moscow State Aviation Institute, Volokolamskoye Shosse 4, GSP, Moscow 125871 Russia

The problems connected with the theory and practice of creation reliable protective coatings for heatstressed elements of structures working under high speed enthalpy oxygen containing gas flows are considered. The main failure sources of coatings under these conditions are revealed and their evaluation criteria are determined. Hazard in commencing an oxidation reaction of the base material under coating is connected with density of open pores and cracks, and partial pressure of the oxidizer. The presence of technological and working defects makes worse the probability character of catastrophic destruction of coating and moves it to a region of much lower value of heat transfer. For the conditions under discussion a physico-chemical model of coating realized in practice for silicide type coating is offered. It provides much faster self-healing of micro-and macrodefects in the coating, blocking of oxidizer supply to pores and cracks by suppression on diffusion in gaseous phase and instantaneous formation of protective oxide film on the working

surface and continuous restoration of scale in erosion entrainment process.

11:25 AM
PREVENTION OF HYDROGEN PERMEATION ON TiAl BY ION IMPLANTATION: Y. Matsumoto[1]; Yao-Can Zhu[1]; Yasuo Suzuki[1]; *Nobuya Iwamoto*[1]; [1]Ion Engineering Research Institute Corporation, 2-8-1,Tsuda-yamate, Hirakata, Osaka 573-0128 Japan

Lightweight intermetallic TiAl is an important alloy for aerospace materials to raise the thrust-to-weight ratio. It has a problem with respect to its resistance to oxidation and hydrogen permeation, especially in the case of hydrogen or methane-burning environment. We have studied the effects of adding several elements, such as Cr, Nb, V and Mn by ion implantation, to prevent hydrogen embrittlement of TiAl at high temperature.

11:45 AM
SILICON CARBIDE COATING ON UO_2 PELLET BY A COMBUSTION REACTION: *Bong Goo Kim*[1]; Y. Choi[2]; Y. W. Lee[1]; D. S. Sohn[1]; [1]Korea Atomic Energy Research Institute, Capsule Development and Utilization, P.O. Box 105, Yusung, Taejeon 305-600 Korea; [2]Sunmoon University, Asan Korea

Multi-layer deposition of silicon carbide and pyrolytic carbon on UO_2 pellet was prepared by using a combustion reaction between carbon and silicon layers. The pyrolytic carbon and silicon layers were deposited by thermal decomposition of propane at 1250ϒC and plasma-enhanced chemical vapor deposition (PE-CVD) of silane at 500ϒC, respectively, followed by a combustion reaction between the two layers. Microstructural observation of the layer with SEM showed that an inner layer existed following the surface contour of the pellet and an outer layer had small amount of fine pores inside. Chemical analysis with EDX and AES revealed that the inner and outer layers were pyrolytic carbon and silicon carbide, respectively. From the TEM observation, the silicon carbide formed during the combustion reaction was fine crystalline beta-silicon carbide. Temperature distribution of the specimen during the combustion reaction was estimated by empirical and numerical methods.

12:05 PM
SUPERHARDNESS EFFECTS IN THE Si_3N_4/TiN CERAMIC NANO-MULTILAYER FILMS: *J. Xu*[1]; Mingyuan Gu[1]; Geyang Li[1]; [1]Shanghai Jiao-Tong University, State Key Lab of MMCs, Shanghai 200030 China

The polycrystalline Si_3N_4/TiN ceramic nano-multilayer films have been synthesized on Si substrates by a reactive magnetron sputtering technique. The primary objective of this research is to investigate the effects of modulation ratio and modulation period on the microhardness and to elucidate the hardening mechanisms of the synthesized nano-multilayer films. The results showed that the hardness of Si_3N_4/TiN nano-multilayers is affected not only by modulation period, but also by modulation ratio. The hardness reaches its maximum value when modulation period equals a critical value L0, which is about 12 nm with a modulation ratio of 3/1. The maximum hardness value is about 40% higher than the value calculated from the rule of mixtures. The hardness of nano-multilayer thin films was found to decrease rapidly with increasing or decreasing modulation period from the point of L0. The microstructure and the internal stress state of the nano-multilayer films have been investigated using XRD and TEM. Based on experimental results, the mechanism of the superhardness in this system was proposed.

INTERCONNECTPACK; INTERCONNECTIONS FOR ELECTRONICS PACKAGING: Structure-Property Relationship and Reliability II

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

Wednesday AM Room: 17A
March 3, 1999 Location: Convention Center

Session Chairs: M. Weiser, Johnson Matthey Electronics; S. Jin, Lucent Technologies

8:30 AM INVITED PAPER
RELIABILITY OF SOLDER JOINTS ON SEVERAL ALTERNATIVE PCB SURFACE FINISHES: *Z. Mei*[1]; F. Hua[1]; J. Glazer[1]; [1]Hewlett Packard Company, Electronic Assembly Development Center, 1501 Page Mill Rd., MS 5L-C, Palo Alto, CA 94304 USA

Electroless Ni coated with immersion Au is being used as an alternative metal finish to Sn-Pb on printed circuit board (PCB). Electroless Ni/electroless Pd/immersion Au is a new metal finish that is being introduced in PCB industry. Mechanical reliability of PBGA (plastic ball grid array) attached on the two metal finishes was studied in both as-received and aged conditions. Weak solder joints on Ni/Au were observed, resulted from a brittle fracture at the interface between Ni-Sn intermetallic compound and electroless Ni. After aging, the solder joint becomes even weaker and more brittle, resulted from the deposition of Au-Sn intermetallic compound at the interface between solder and Ni-Sn compound. The Ni/Pd/Au finish provided an improved solder joint reliability in some conditions, which is probably related to the Sn-Pd intermetallic compound formation. Some results on immersion Ag, immersion Sn, and electroless Pd on Cu or Ni may be presented at the conference, if data are available by then.

9:00 AM
MANUFACTURING FEASIBILITY AND RELIABILITY OF LOW MELTING SOLDERS: *F. Hua*[1]; Z. Mei[1]; J. Glazer[1]; [1]Hewlett-Packard Company, Electronic Assembly Development Center, 1501 Page Mill Rd., Palo Alto, CA 94304 USA

The applications of low melting, Sn-Bi and Sn-Bi-Pb based solders in electronic products were studied with the emphasis on manufacturing related issues and solder joint reliability. The melting temperatures and basic mechanical properties were determined as an initial screening assessment of viable candidate for further prototype development. Prototype products are printed circuit boards (PCBs) with organic coated Cu surface finishes, soldered with components with different lead frame metals, Sn-Pb on Alloy 42, Sn-Pb on Cu, Pd/Ni on Cu, Au on Ni-Cu. Visual inspection of solder joint, push and pull of component leads, shock, vibration or prototype production boards were conducted. An environmental thermal cycling chamber was used to test the thermal mechanical reliability of the solder joints. The fracture surface and cross section of solder joints were analyzed for failure mode and bonding intermetallic compounds. It is concluded that low temperature solders, along with correct selections of soldering flux and component lead surface finishes, could be viable solutions for electronic assembly.

9:25 AM INVITED PAPER

HIGH MILEAGE SOLDER JOINT RELIABILITY OF ALTERNATOR POWER DIODE ASSEMBLY: S. C. White[1]; E. L. Lutz[1]; *T. Y. Pan*[2]; H. D. Blair[2]; J. M. Nicholson[2]; [1]Visteon Powertrain Control Systems, Textile and McKean Rds., Ypsilanti, MI 48197 USA; [2]Ford Motor Company, Ford Research Laboratory, 20,000 Rotunda Dr., P.O. Box 2053, Bldg. R, M/D 3135, Dearborn, MI 48121-2053 USA

The reliability of the solder joints at the power diode leads to the rectifier in automotive alternators are required to last at least 10 years / 150,000 miles. The service environment of the alternator and the heat generation of the diodes themselves provide a great challenge to the solder joint reliability. The ambient service temperature of the alternator can get to 175°C and the internal diode can run as hot as 205°C. The solder joints have been and are assembled by a wave soldering process using a Pb-free Sn-Ag eutectic solder since the late 80's, and constitutes one of the very first Pb-free solder assemblies in mass production (5.5 million parts a year) in the industry. A recent introduction of a new diode, from a different supplier, was required to avoid a projected supply interruption and a significant cost increase. However, the new diode rectifier assemblies were shown to have poor lead wire solder joint thermal cycle reliability. It was discovered that the high thermal dissipation of the new diodes, normally a desirable feature, resulted in poor solder joint reliability. A cross-organizational team, utilizing advanced analytical tools, made a patent-pending rectifier leadframe design change which resulted in a dramatic increase in solder joint thermal cycle fatigue life while maintaining best-in-class rectifier package dimensions. The team achieved first-pass prototype success while using existing production facilities and still met aggressive launch timing.

9:55 AM

EFFECTIVE MICROALLOYING FOR THE IMPROVEMENT OF THERMAL FATIGUE AND CREEP RESISTANCE IN EUTECTIC Sn-Pb SOLDERS: N. Wade[2]; T. Akuzawa[3]; S. Yamada[2]; D. Sugiyama[2]; I-S. Kim[1]; *K. Miyahara*[1]; [1]Nagoya University, Dept. of Molecular Design and Eng., Nagoya 464-01 Japan; [2]TOPY Industrial, Ltd., Technical R&D Lab., Toyohashi Japan; [3]Nippon Filler Metals, Chiba Japan

This study aims to improve the thermal fatigue and creep resistance of Sn-Pb eutectic solder by the addition of small amount of effective elements, such as Sb, Ag, Cu and In, which are selected by preliminary experiments and statistical analysis. Thermal fatigue test was performed under the heat cycling of 233 to 393K. Creep tests were conducted at the stress and temperature range of 5 to 15 MPa and 313 to 378K. The above microalloying improved significantly the thermal fatigue life and creep life. For instance, the fatigue life for 50% crack generation was improved by twice and the creep life at 10 MPa and 353K by ten times. Transmission electron microscope observation indicated that the excellent properties came from the precipitation hardening by an appropriate combined addition of the microalloying elements.

10:20 AM BREAK

10:30 AM INVITED PAPER

ROLE AND RESPONSE OF Sn-Pb MICROSTRUCTURE IN CONSTITUTIVE MODEL-BASED PREDICTIONS OF SOLDER JOINT THERMAL MECHANICAL FATIGUE: *P. T. Vianco*[1]; S. N. Burchett[1]; M. K. Nielsen[1]; [1]Sandia National Laboratory, P.O. Box 5800, MS 1411, Albuquerque, NM 87185-1411 USA

The capability to measure the extent of thermal mechanical fatigue in solder is an important milestone towards predicting the reliability of solder interconnects in electronics. Theoretical and experimental research has resulted in the development of a constitutive model for Sn-Pb solder, which when coupled with a finite element code, provides such an avenue for quantifying microstructural damage to Sn-Pb solder during thermal mechanical fatigue. The constitutive model based on two-term, power-series expression, each term explicitly representing the contributions of time-dependent and time-independent plastic deformation on the performance of the solder under thermal mechanical loading. An important response by the model is its description of the evolution of the solder microstructure during the course of thermal mechanical fatigue processes. Specifically, the model/code describes both spatial as well as temporal changes to the Pb-rich phase particle distribution in the Sn-Pb alloy that comprises the joint; the extent of such changes are believed to be the precursor to crack initiation and eventually, crack propagation and failure of the solder joint. The role of the Pb-rich phase particle size characterizing the starting microstructure of through-hole solder joints has been investigated. The spatial distribution of particle sizes in the range of $3x10^{-6}$ mm^2 to $20x10^{-6}$ mm^2, as determined from experimental studies, represented the starting microstructure input for the model. The Pb-rich phase size was distributed non-homogeneously in the solder joint; the effects of these distributions on fatigue damage and likely initiation sites of cracks will be described. The resulting microstructural development, as predicted by the model, will be evaluated and compared with available experimental observations. The sensitivity of thermal mechanical fatigue damage to the materials and joint geometries, as ameliorated or aggravated through the solder microstructure, will also be documented. [1]Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Dept. of Energy under contract DE-AC04-94AL85000.

11:00 AM

THE INFLUENCE OF TEMPERATURE ON FATIGUE-CREEP INTERACTIONS IN A LEAD-TIN SOLDER ALLOY: *W. J. Plumbridge*[1]; J. E. Moffatt[1]; [1]The Open University, Dept. of Mats. Eng., Milton Keynes MK7 6AA UK

Strain-controlled fatigue test, involving dwells at maximum strain limits, have been performed on bulk specimens of a eutectic lead-tin solder alloy at room temperature at 75°C. During continuous cycling, softening occurs at each temperature to around 10 and 15 percent respectively. The fatigue endurance is reduced by typically one third at the higher temperature. The incorporation of a dwell of 10 or 100s into the cycle causes a reduction in fatigue life in comparison to that observed during continuous cycling. Cycles containing balanced dwells at maximum and minimum strain limits are the most deleterious when lifetime debits of up to fivefold are observed at both temperatures. Unbalanced compression-only profiles tend to be the least damaging. The stress relaxation characteristics are similar in all dwells. Metallographic observations of sectioned specimens reveals surface and intergranular cracking which is accentuated at higher-strain ranges and temperature but not dramatically affected by the cycle shape. These findings are considered in terms of the behavior of other engineering alloys and potential lead-free replacement solders.

11:25 AM

EFFECT OF STRAIN RATE AND HOLD TIME ON THE ISOTHERMAL FATIGUE LIFE OF Sn-3.5Ag-X(X=Bi, Cu, In) SOLDER ALLOYS: *Yoshiharu Kariya*[1]; Masahisa Otsuka[1]; [1]Shibaura Institute of Technology, Dept. of Mats Engineering, Shibaura 3-9, Minato-ku, Tokyo 108-8548 Japan

Strain rate and hold time are most important factors affecting fatigue life of solder alloys. However, no systematic studies have been carried out with respect to the influence of these parameters on fatigue properties of lead-free solders, while sufficient data are available for eutectic Sn-Pb solder. In our previous study, we clarified the effect of third element (Bi, Cu, and In) on the fatigue life of Sn-3.5%Ag binary alloy at moderately high strain rate and found that the fatigue life of Sn-3.5Ag binary alloy remarkably decreased with increasing content of bismuth though the addition of copper and indium slightly decreased the fatigue life of Sn-3.5% Ag alloy. In this paper, the effect of strain rate and tensile hold time on the isothermal fatigue life of bulk Sn-3.5%Ag-X(X=Bi, Cu and In) solder alloys have been studied with loading mode of sawtooth and trapezoid wave. Low strain rate is found to reduce the fatigue life of Sn-3.5%Ag-X. Increase in hold time at maximum strain also decreases the fatigue life of these ternary alloys, though holding for more than 2 minutes results in almost constant fatigue life. This should be ascribed to creep which occur during holding and low strain rate deformation. The result coincides well with the fact that applied stress has fully relaxed with 2 minutes even at room temperature. However, the fatigue life itself is found to be insensitive to hold time.

11:50 AM INVITED PAPER

CHARACTERIZING THE WEAK ORGANIC ACIDS USED IN LOW SOLIDS FLUXES: B. A. Smith[1]; *L. J. Turbini*[1]; [1]Georgia Insti-

tute of Technology, Dept. of Mats. Sci. Eng., 778 Atlantic Dr., Atlanta, GA 30332-0245 USA

The elimination of chloroflurocarbons (CFC's) and other chlorinated cleaning solvents due to their long-term environmental impact has lead electronic assemblers to examine soldering fluxes that reduce or eliminate the need for post-solder cleaning. Today, low solids fluxes are replacing more traditional rosin-based and water-soluble fluxes because many of them can be used in a non-clean process. Most low solids fluxes use weak organic acids as active ingredient. It has been reported that some of these weak organic acids leave behind residues that are corrosive to copper. Surface Insulation Resistance (SIR) measurements of flux-processed comb patterns have been the main test method used to determine the corrosivity of flux residue. This test has been performed with test samples exposed to accelarated temperature and humidity conditions of 85°C and 85%RH and a 50V bias. Recent data on some weak organic acids suggests that they slowly disappear at this temperature and a lower test temperature of 65°C has been introduced into the new Bellco Standard. In Europe, this test is normally performed at 40°C and 93%RH. This paper will report on the application of SIR test to study the corrosive behavior of six carboxylic acids that are commonly used as the active ingredients in soldering fluxes. Coupons treated with equimolar solutions of the acids were either exposed to reflow-soldering conditions or wave soldered face-up to create partially heated residues. Both tests were run under two different accelerating conditions, the first being 85°C/85%RH for 7 days and the second being 40°C/93%RH for 20 days. This latter condition is being considered for inclusion in an ISO standard. At the end of the test period, both corrosion and SIR test samples were examined under a microscope and any residues or dendritic growth were documented. SEM and EDX characterization was also performed to determine the residue and dendrite composition.

INTERNATIONAL SYMPOSIUM ON ADVANCES IN TWINNING: Twinning in Intermetallics

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

Wednesday AM Room: 17B
March 3, 1999 Location: Convention Center

Session Chairs: A. K. Vasudevan, Office of Naval Research, 800 N. Quincy St., Arlington, VA 22217-5660 USA; Terence E. Mitchell, Los Alamos National Laboratory, Center for Mats. Sci., Los Alamos, NM 87545 USA

8:30 AM INVITED PAPER

MICROMECHANISMS OF TWIN NUCLEATION IN TiAl: EFFECTS OF NEUTRON IRRADIATION: *Man H. Yoo*[1]; A. Hishinuma[2]; [1]Oak Ridge National Laboratory, Metals and Ceramics Division, P.O. Box 2008, Oak Ridge, TN 37831-6115 USA; [2]Japan Atomic Energy Research Institute, Dept. of Materials Science and Engineering, Tokai Research Establishment, Tokai, Ibaraki-ken 319-11 Japan

In Ti-47at%Al alloys of the duplex microstructure, consisting of equiaxial grains of the Ti_3Al and TiAl phases, an increase in tensile elongation at 873 K from 6% to 10% was reported after neutron irradiation to a dose of 1 x 10^{20} n-cm^{-2} (E > 1 MeV). This so-called radiation-induced ductility (RID) is attributed to the formation of effective twin embryos in the presence of interstitial-type Frank loops in γ-TiAl phase and the subsequent nucleation and growth of microtwins during post-irradiation plastic deformation. In this paper, micromechanics of defect clustering under irradiation and twin formation during deformation are analyzed. The results are given on the stability of Frank loops against unfaulting, the source operation of twinning partial dislocations, and the critical conditions for twin formation. The RID phenomenon will be elucidated from a viewpoint of the proposed micromechanisms and the TEM analyses of the irradiation-induced microstructure. [Research sponsored by the Division of Materials Sciences, U.S. Department of Energy under contract number DE-AC05-96OR22464 with Lockheed Martin Energy Research Corp.]

9:05 AM

INTERFACE CONTROLLED DEFORMATION TWINNING IN TWO-PHASE TiAl WITH A LAMELLAR MICROSTRUCTURE: *Luke M. Hsiung*[1]; T. G. Nieh[1]; [1]Lawrence Livermore National Laboratory, Mats. Sci. and Tech., L-369, P.O. Box 808, Livermore, CA 94551-9900 USA

Mechanisms of deformation twinning in creep-deformed lamellar TiAl (γ) - Ti3Al (α2) have been investigated. Since the operation and multiplication of lattice dislocations within both //0032/ and α2 lamellae are very limited due to a refined lamellar microstructure (γ lamelae: 100 - 300 nm thick, α2 lamellae: 10 - 50 nm thick), the glide of preexisting interfacial dislocations (i.e. interfacial sliding) becomes a dominant deformation mode. During the gliding of interfacial dislocations along the lamellar interfaces, their mobility can be impeded by obstacles such as impinged lattice dislocations. This event increases as applied stress or strain increases and subsequently resulting in the pile-up of interfacial dislocations. When the alloys are crept at a high stress level, deformation twinning is found to become a predominant deformation mode with the deformation twins preferentially nucleating from lamellar interfaces. It is suggested that deformation twinning is a stress relaxation process for dissipating stress concentration at the head of each dislocation pile-up. A twinning formation mechanism driven by the pile-up of interfacial dislocations is accordingly proposed and verified. This work was performed under the auspices of the U.S. Department of Energy by LLNL under contract No. W-7405-Eng-48.

9:30 AM INVITED PAPER

DEFORMATION TWINNING IN A HfV2 + Nb - BASED LAVES PHASE ALLOY: Yoshisato Kimura[1]; *David E. Luzzi*[1]; David P. Pope[1]; [1]University of Pennsylvania, Dept. of Mats. Sci. and Eng., 3231 Walnut St., Philadelphia, PA 19104-6272 USA

Single phase HfV_2, like other cubic C15 Laves phases, shows almost no plasticity at low temperatures. Nb additions are known to improve the ability of this material to deform by mechanical twinning, however single phase material remains extremely brittle. Two-phase alloys consisting of the C15 HfV_2 + Nb phase and a bcc (V, Nb) solid solution exhibit considerable ductility (3% plastic strain at ambient temperature), even though the alloy has the brittle C15 matrix. To investigate the deformation behavior of this two phase alloy, compression tests were conducted at low temperatures, down to 4.2K. The 0.2% flow stress drops dramatically at around 77K - it is nearly 500 MPa lower at 77K than it is at 300K - then rises rapidly at temperatures below 77K. No such anomaly is seen in samples with less than 20% volume fraction of C15. Transmission electron microscopy revealed that substantial mechanical twinning takes place in the C15 phase at room temperature and at 77K, but not at 4.2K. This lack of twinning at 4.2K suggests that mechanical twinning in the C15 is both a stress- and temperature-driven phenomenon. We believe that the cause of the drop in flow stress at 77K is an increased ease of mechanical twinning in the C15 phase of the two phase alloy.

10:05 AM BREAK

10:15 AM INVITED PAPER

TRANSMISSION OF TWINNING AND SLIP AT LAMELLAR INTERFACES IN Ti-Al: *Peter M. Hazzledine*[1]; [1]UES, Inc., 4401 Dayton-Xenia Rd., Dayton, OH 45387 USA

Twinning is an important plastic mechanism in the gamma phase of lamellar Ti-Al at all temperatures. It may contribute both to soft mode and to hard mode deformation. Lamellar Ti-Al is an interface strengthened material in which deformation must be propagated across domain boundaries in the gamma phase during soft mode deformation and across

both gamma-gamma and alpha-gamma lamellar interfaces during hard mode deformation. The domain boundaries and the gamma-gamma lamellar boundaries may or may not themselves be twin interfaces. This paper examines the mechanisms of deformation transmission e.g. a hard mode twin in one lamella triggering slip in the neighboring lamella and attempts to calculate the contribution made to the Hall-Petch strengthening by such mechanisms.

10:50 AM INVITED PAPER

TWINNING IN $ReSi_{2-x}$: *Terence E. Mitchell*[1]; Amit Misra[1]; [1]Los Alamos National Laboratory, Center for Materials Science, MS-K765, P.O. Box 1663, Los Alamos, NM 87545 USA

$ReSi_{2-x}$ is usually referred to as rhenium disilicide but it actually has a stoichiometry of $ReSi_{1.75}$. Also it is usually described as having the tetragonal $MoSi_2$ C11b structure but in fact it exhibits a number of incommensurate and commensurate structures which are based on the C11b structure. Structure A has an incommensurate periodicity of 4.14a along the a axis. It has a small orthorhombic distortion (b/a~1.005) accompanied by twinning on the (110) plane and a small monoclinic distortion ($b\sim90.2_o$ accompanied by twinning on the (001) plane. Structure B is also incommensurate but has a larger monoclinic angle of 107_o; B appears to result from a shear transformation of A, giving rise to (001) twins. Prolonged annealing at high temperatures results in structure C which is commensurate and has planes parallel to, and exactly 4 times the spacing of, the(101) planes of the underlying C11b structure. Structure C is also twinned. The various structures are apparently caused by attempts to accommodate the Si structural vacancies. The relationship between these structures and the Nowotny "chimney-ladder" structures which have the general formula M_nSi_{2n-m} and are based on the $TiSi_2$ structure will be discussed.

INTERNATIONAL SYMPOSIUM ON GAMMA TITANIUM ALUMINIDES: TiAl Alloys: Flow and Fracture

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

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

Wednesday AM Room: 8
March 3, 1999 Location: Convention Center

Session Chairs: Michael V. Nathal, Nasa Lewis Research Center, Cleveland, OH MS 49-3 USA; Gilbert Henaff, LMPM-ENSMA, Teleport 2, Futuroscope Cedex F-86960 France

8:30 AM INVITED PAPER

ASSURING RELIABILITY OF GAMMA TITANIUM ALUMINIDES IN LONG-TERM SERVICE: *James M. Larsen*[1]; Andrew H. Rosenberger[1]; Kezhong Li[2]; *Reji John*[2]; David C. Maxwell[2]; *W. J. Porter*[2]; [1]Air Force Research Laboratory, Materials & Manufacturing Directorate, AFRL/MLLN, Wright-Patterson Air Force Base, OH 45433-7817 USA; [2]University of Dayton Research Institute, 1031 Irving Ave., Dayton, OH 45419-0128 USA

Gamma TiAl alloys offer the potential for major reductions in weight of turbine engine components, if higher-density materials can be replaced without sacrificing long-term reliability in service. To assess this potential, an overview is presented of the structural capabilities available from gamma titanium aluminide alloys. Emphasis is given to effects of material defects, mechanistic aspects of fatigue damage evolution, and the roles of high-temperature, time-dependent deformation and environmental effects. Although gamma alloys exhibit excellent fatigue strengths, in many applications the material's resistance to service-induced damage is a critical concern. In turbine engines, such damage may result from impacts by foreign objects in the flow path. In addition, numerous components in turbine engines are subject to both low- and high-cycle fatigue. To predict the range of behavior that may be expected for gamma titanium aluminides requires consideration of damage tolerance, specifically addressing the potential for growth of small fatigue cracks that may form under a variety of circumstances. Approaches for life prediction in these materials are discussed, emphasizing the roles of fatigue crack initiation and growth. In addition, an attempt is made to assess the strengths and limitations of these materials with respect to application requirements and to suggest avenues for improvements in the balance of mechanical properties.

9:00 AM

THREE CHARACTERISTIC PHASES OF FATIGUE CRACK GROWTH IN A TiAl BASED ALLOY: *Ze-Wen Huang*[1]; Paul Bowen[2]; [1]Birmingham University, IRC Centre in Materials, Edgbaston, Birmingham, West Midlands B15 2TT UK; [2]Birmingham University, School of Metallurgy and Materials, Edgbaston, Birmingham, West Midlands B15 2TT UK

The fatigue crack growth behaviour of a g-TiAl based Ti-48Al-2Mn-2Nb alloy has been studied at room temperature in air. Three distinct phases of fatigue crack growth were found commonly for the fully lamellar microstructures of 550 micrometer colony size. Fatigue crack initiation and early growth near threshold, as the first phase, proceeded at a very slow growth rate along a mode I crack direction. There is no crack deflection, and no intact ligaments are left in the crack wake during this growth. The second phase is characterised by intermediate growth rates and a non-linear variation of log da/dN with log DK, and this gives a wide range of crack growth rates and behaviour quite different from that observed in conventional alloys. Now there may be some crack deflection and small ligaments can be found in the crack wake. These two regimes account for ~ 95% of the total number of cycles to failure while the crack propagates a relatively short distance. The third phase is typically demonstrated to be a regime of catastrophic propagation. Most of the fatigue crack area observed derives from this very fast crack growth process, where a higher degree of crack deflection, branching and unbroken ligaments can be found. Extensive SEM examination has been carried out to correlate this mechanical behaviour with fractographic features. The mechanisms governing these three distinct crack growth phases will be discussed in terms of the underlying microstructures.

9:20 AM INVITED PAPER

THE VARIABILITY OF TENSILE PROPERTIES IN CAST GAMMA TITANIUM ALUMINIDES: Rafael Raban[1]; *Tresa M. Pollock*[1]; [1]Carnegie Mellon University, MSE Dept., 5000 Forbes Ave., Pittsburgh, PA 15213 USA

The use of investment cast gamma titanium aluminides in aircraft engine applications requires that some degree of tensile ductility be achieved reproducibly. Factors influencing the variability of tensile properties in several cast TiAl alloys have been investigated. Alloys include Ti-48Al-2Cr-2Nb, Ti-46.5Al-2Cr-2Nb, Ti-47Al-2Cr-2Nb+0.5at%B and Ti-45Al-2Cr-2Nb+0.9at%B. The variability of room temperature yield strength and tensile ductility within individual cast plates will first be discussed. Additionally, variations in properties across a range of casting conditions will be presented along with associated changes in microstructure for each alloy. Fractographic observations, common features of the failure process and factors which may reduce variability will be discussed.

9:50 AM

MICROSTRUCTURAL STRENGTHENING OF FULLY LAMELLAR Ti-Al ALLOYS: Peter M. Hazzledine[1]; *Dennis M. Dimiduk*[1]; [1]Air Force Research Laboratory, Materials and Manufacturing Directorate, Wright-Patterson AFB, OH 45433 USA

Fully lamellar Ti-Al alloys with fine lamellae have exceptional yield strengths at low temperatures while retaining attractive high temperature properties. The four most significant microstructural parameters

governing these mechanical properties are the average lamellar thickness, the distribution of lamellar thicknesses, the volume fraction of alpha 2 (or the number fraction of gamma/alpha 2 interfaces) and the grain size. A predictive theory of the Hall-Petch strengthening would include these parameters and take account of the extreme plastic anisotropy of the constituent lamellar grains. In addition, to describe recent very high strength alloys, the theory must include the effects of strength saturation and which become important in lamellae < 20 nm thick. This paper reports progress towards such a theory and compares it with experimental measurements.

10:10 AM

DYNAMIC TENSILE PROPERTIES OF Ti-47Al-2Mn-2Nb ALLOY: *Dongliang Lin*[1]; Wang Yu[1]; [1]Shanghai Jiao Tong University, Institute of Mats. Sci. & Eng., 1954 Haushan Rd., Shanghai 200030 PR China

Room-temperature tensile properties of polycrystal Ti-47Al-2Mn-2Nb alloy with near lamellar (NL) microstructure were investigated at the strain rates between 10-5 and 1000s-1 using conventional testing machine and a self-designed Split-Hopkinson tensile bar setup with a rotating disk. It is found that tensile ductility varies within a narrow range with the strain rate while dynamic strengths (sd) of the alloy are obviously higher than static strengths (ss). There exists linear relationship between ss and the logarithm of the strain rate (ln) while linear relationship exists between sd and the strain rate itself ( ). Fractography analysis indicates that the alloy fractures in a mixed mode of predominant transgranular cleavage and minor intergranular failure under static and dynamic strain rates. Environmental effect is excluded from the main cause for the room-temperature brittleness of the investigated alloy.

10:30 AM INVITED PAPER

THE CONTRASTING ROLE OF MICROSTRUCTURE IN INFLUENCING THE GROWTH OF LARGE AND SMALL FATIGUE CRACK IN TiAl ALLOYS: *Robert O. Ritchie*[1]; J. J. Kruzic[1]; J. P. Campbell[1]; [1]University of California, Berkeley, Dept. of Mats Sci and Mineral Eng, 463 Evans Hall #1760, Berkeley, CA 94720-1760 USA

The initiation and growth behavior of small (<500 μm) surface cracks in a γ-based TiAl alloy, of composition Ti-47Al-2Nb-2Cr-0.2B (at.%), has been studied in both duplex (average grain size ~150 μm) microstructures, with results compared to the corresponding behavior of long (>3 mm) though-thickness cracks. Small crack experiments were carried out in four-point bending with cracks both initiated naturally and from created defects; large-crack tests were performed with compact-tension samples. Results indicated that whereas the lamellar microstructures displayed far superior "large crack" fatigue-crack growth properties, growth-rate data from the small-crack experiments were similar for the two microstructures. Such results are interpreted in terms of the suppression of extrinsic toughening, in this alloy from crack closure and uncracked (shear) ligament bridging, with cracks of limited size. In light of the similarity in intrinsic fatigue-crack growth resistance, the higher crack-initiation res istance and the reduced extent of scatter for the finer-scale duplex structure, this microstructure is preferred to the tougher lamellar structure for most fatigue-crack applications.

11:00 AM

HIGH TEMPERATURE CRACK GROWTH IN A GAMMA TiAl ALLOY UNDER CONSTANT-CREEP-LOADING CONDITIONS: *Kumar Jata*[1]; *Young-Won (Y-W.) Kim*[2]; [1]Air Force Research Laboratory, AFRL/MLLM, Bldg. 655, Wright-Patterson AFB, OH 45433 USA; [2]UES, Mats. Development & Processes Div., 4401 Dayton-Xenia Rd., Dayton, OH 45432 USA

Crack growth behavior of a gamma titanium aluminide alloy, K5 (Ti-46Al-2Cr-3Nb-0.2W-0.2Si), was investigated under constant-loading conditions in a nearly fully-lamellar (NFL) microstructural form at 650 and 800ϒC. The NFL microstructure consisted of 400 μm size lamellar grains containing a small volume fraction of finely (5-20 μm) dispersed gamma grains. Both crack opening displacement (COD) and crack extension were measured as functions of holding time and apparent stress intensity factor. Results show that the COD changes with time are closely related to the creep deformation previously measured on the same material. Cracking occurred following the creep deformation/damage in the plastic zone and ensued at stress intensities much higher than that for fracture initiation toughness. At 650ϒC, crack extension occurred through microcracking (lamellar separation) and then fracture of the translamellar ligaments. At 800ϒC, the major crack propagates primarily along the boundary (lamellar and grain) areas, frequently resulting in dimpled fracture surfaces which may be caused by void formation. Analysis will be made on the complex relationships between the crack-tip area deformation (both instantaneous and creep), crack propagation, microstructure, and boundary weakening.

11:20 AM INVITED PAPER

FATIGUE CRACK GROWTH THRESHOLDS OF TiAl ALLOYS: *Kwai S. Chan*[1]; [1]Southwest Research Institute, Mats. and Structures, 6220 Culebra Rd., San Antonio, TX 78238 USA

The growth behavior of fatigue cracks in TiAl alloys have been shown to depend on the crack size. Most of the naturally nucleated small fatigue cracks have been found to arrest after nucleation. Only a few do propagate at stress intensity ranges below the large crack threshold. The objective of this paper is to review the current understanding of this small crack behavior and to explore the validity of the concept of a growth threshold for small cracks, defined in terms of the applied stress range and the crack length at which crack arrest occurs, for treating the growth/no growth of small cracks. Crack growth threshold values for small cracks in TiAl alloys are presented and compared against the large crack value. The possible application of a size-dependent threshold for predicting of fatigue crack growth in TiAl alloys is discussed and evaluated against laboratory data.

11:50 AM

INFLUENCE OF FOREIGN OBJECT DAMAGE ON THE ELEVATED TEMPERATURE FATIGUE RESPONSE OF GAMMA TITANIUM ALUMINIDE ALLOYS: *Trevor S. Harding*[1]; J. Wayne Jones[1]; Paul S. Steif[2]; Volus McKenna[2]; James M. Larsen[3]; Andrew H. Rosenberger[3]; [1]University of Michigan, Dept. of Mats. Sci. and Eng., 2105 H.H. Dow Bldg., 2300 Hayward St., Ann Arbor, MI 48109-2136 USA; [2]Carnegie Mellon University, Mechanical Engineering, Scaife Hall, Pittsburgh, PA 15213 USA; [3]Air Force Research Laboratory, Materials and Manufacturing Directorate, Wright Patterson Air Force Base, OH 45433 USA

The high specific stiffness and strength of gamma TiAl alloys has made them leading candidates for use in weight-critical components including turbine blades. The effects of service induced damage events, such as foreign object damage (FOD), on the fatigue behavior of gamma TiAl is of great importance for transition of this class of materials into gas turbine engines. In the present study simulated FOD impact tests were conducted on three cast gamma TiAl alloys, Ti-47.9Al-2.0Cr-1.9Nb, Ti-47.3Al-2.2Nb-0.5Mn-0.4W-0.4Mo-0.23Si and Ti-47Al-2Nb-0.8vol.%TiB2. Impact sites were subsequently characterized in terms of types and severity of damage present on the specimen surface. Fatigue failure stress was determined using an incremental step loading fatigue test conducted in air at 600°C. Correlations between severity of impact damage and fatigue failure stress will be discussed in terms of a threshold-based model. Fractographic analysis was used to reveal the mechanisms of initial damage and crack propagation, as well as, the shape and size of internal damage. These results are then correlated with the threshold-based approximation of fatigue failure stress. Further modeling and analysis of the role of near-threshold and small crack growth from impact damage sites in terms of estimated lifetime will be discussed.

12:10 PM

MIXED MODE CRACK GROWTH IN GAMMA TiAl: *Reji John*[1]; W. John Porter[1]; Andy Rosenberger[2]; [1]University of Dayton Research Institute, 300 College Park, Dayton, OH 45322 USA; [2]AFRL/MLLN, Wright-Patterson AFB, Dayton, OH 45433 USA

Gamma TiAl alloys are under consideration for use as engine blade materials in advanced aerospace engines. In these components, stage I crack growth can be expected to occur under mixed mode (mode I + mode II) loading at locations such as the root of the blade. The "brittle" behavior of Gamma TiAl at low temperatures (steep da/dN versus ΔK) necessitates characterization of the near-threshold behavior under service loading conditions. Hence, a program was initiated to investigate the effect of mixed mode loading on the near-threshold behavior of a Gamma TiAl alloy (identified as 395). A centrally notched disk specimen was used to conduct the tests at room and elevated temperatures.

Unique tests were also conducted using specimens with large (approx. 5mm), centrally located grains to characterize the interlamellar growth. This presentation will discuss the mode mixity effects on the interlamellar and intralamellar crack growth behavior of Gamma TiAl.

LONG TERM STABILITY OF HIGH TEMPERATURE MATERIALS: Stability of Ni-base Alloys - I

Sponsored by: Structural Materials Division, High Temperature Alloys Committee, Physical Metallurgy Committee
Program Organizers: Gerhard E. Fuchs, Lockheed Martin Corporation, Schenectady, NY 12301-1072 USA; Kathryn A. Dannemann, Southwest Research Institute, San Antonio, TX 7828-0510 USA; Todd C. Deragon, Special Metals Corporation, New Hartford, NY 13413-5392 USA

Wednesday AM Room: 9
March 3, 1999 Location: Convention Center

Session Chair: Gerhard E. Fuchs, University of Florida, Dept. of Mats. Sci. and Eng., Gainesville, FL 32611-6400 USA

8:30 AM KEYNOTE
THE STABILITY OF SUPERALLOYS: *S. T. Wlodek*[1]; [1]Gamma Prime Consultants, 17810 Pueblo Vista Lane, San Diego, CA 92127-1272 USA

Any structure that is exposed to temperatures, different from those at which that structure was previous equilibrated, will change so as to achieve the form that is stable at that temperature. A change in the structure sensitive properties of that material will then result. This review summarizes such reactions for the superalloy family of alloys, used in gas turbines. The superalloy family of compositions, whether based on nickel, cobalt or nickel-iron systems, is not immune to such property changes. Indeed, due to their high service temperatures, these alloys usually exhibit large changes in their structure sensitive properties during normal service. Properties that can be so affected include: tensile strength and ductility, creep, rupture, rupture ductility and all modes of fatigue, including crack growth rates. These changes in properties can be major. Nevertheless, the design community continues to design on the basis of as-heat treated properties. A better appreciation of the importance of structural stability remains one area through which further improvements in superalloy properties can still be achieved. This paper reviews the structural changes that can occur in all of the components of a superalloy. These include the precipitation of unwanted topological-closed packed phases and other intermetallics, change in carbides and boride structures, and changes in the amount and morphology of gamma prime (γ') and similar strengthening precipitates. The treatments of the approaches that have been developed to predict, or control such structural changes is included, and where possible, the effect of such changes have on properties is documented. The available data on the long time stability of superalloys is summarized in tabular form, listing the published studies on stability, nature of the precipitation reactions, and documented effects on properties for each commercial alloy. The morphology of major structural changes is illustrated. If the structural changes that an alloy undergoes in service, particularly the size and amount of γ' and γ", are characterized, such data can be used to estimate the service temperature that the engine component encountered. The techniques for estimating service conditions, from such measurements, so useful in failure analysis, are presented.

9:10 AM INVITED PAPER
LONG-TERM MICROSTRUCTURAL STABILITY OF SINGLE CRYSTAL SUPERALLOYS: *W. S. Walston*[1]; [1]GE Aircraft Engines, One Neumann Way, Cincinnati, OH USA

Long-term microstructural stability is a key parameter in the development and application of single crystal superalloys to gas turbine engines. The formation of topologically close packed (TCP) phases occurs to some degree in most single crystal superalloys. The effect of these phases on properties will be discussed. In addition, the effects of time and temperature on the formation of TCP phases will be shown for recent single crystal superalloy, including René N6. Another form of microstructural instability has recently been observed in high refractory content single crystal superalloys. This instability, termed SRZ, is a cellular phase transformation that can occur either beneath coatings or in the alloy substrate. The occurrence and effects of this instability in various alloys will be discussed. The third form of microstructural instability observed in several single crystal superalloys is the conversion of the γ matrix with γ' precipitates to a microstructure with a continuous γ' phase. Several examples of this behavior will be shown. The relationship between this form of instability, rafting and creep rupture properties will also be discussed.

9:40 AM
THERMAL STABILITY OF HIGH TEMPERATURE STRUCTURAL ALLOYS: *R. K. Rasefske*[1]; A. Castagna[1]; C. E. Jordan[1]; [1]Lockheed Martin, P.O. Box 1072, Schenectady, NY 12301-1072 USA

High temperature structural alloys are under evaluation for numerous applications which require long term operation at elevated temperatures. The effect of elevated temperature exposure on the microstructure and mechanical properties of a number of alloys was characterized. Iron-based alloys (330 stainless steel, 800H and MA 956) and nickel-based alloys (Hastelloy X, Haynes 230, 718 and MA 754) were evaluated for room temperature tensile and impact toughness properties after exposure at 750°C for 10,000 hours. Of the iron-based alloys evaluated, Alloy 800H showed the greatest degree of primary carbide coarsening and a corresponding reduction in ductility and toughness as compared to the unexposed condition. Within the group of nickel-based alloys tested, Alloy 718 showed the most dramatic change in structure as it formed delta phase during the long time exposure at 750°C with significant reductions in strength, ductility, and toughness. Haynes 230 and Hastelloy X showed significant carbide precipitation and a resulting reduction in ductility and toughness. Haynes 230 was also evaluated for room temperature tensile and impact toughness properties after 10,000 hours of exposure at 480°, 590°, 850°, 950° and 1050°C. Microstructural evaluation showed that extensive precipitation of $M_{23}C_6$ carbides occurred at 590°C. At 750°C the precipitates of $M_{23}C_6$ carbides coarsened, and primary M_6C carbides were found to be W and Mo rich, and contain little Cr. For exposures above 850°C, the M_6C carbides changed morphology from blocky to a more irregular type shape. Mechanical testing of the thermally exposed Haynes 230 specimens indicated relatively small reductions in ultimate tensile strength and yield strength over the range of exposure temperatures studied, however, large reductions in impact strength were evident after exposure at temperatures of 750°C and above.

10:00 AM
THE EFFECT OF LONG TERM ISOTHERMAL EXPOSURE ON THE MICROSTRUCTURE AND PROPERTIES OF INCONEL® ALLOY 783: *Sarwan Mannan*[1]; John deBarbadillo[1]; Stanley Gregory[1]; [1]Inco Alloys International, Inc., 3200 Riverside Dr., Huntington, WV 25705-1771 USA

Recently developed INCONEL® alloy 783 (nominal composition of Ni-34Co-26Fe-5.4Al-3Nb-3Cr) is precipitation strengthened by Ni3Al-type Gamma Prime and NiAl-type Beta phases. Due to its low coefficient of thermal expansion, high strength, and good oxidation resistance, alloy 783 was designed for use in aircraft gas turbine components such as rings, casings, shrouds, and seals and has been considered for use in a number of other critical industrial turbine components. In this study, commercially produced alloys 783, 718 and 909 were annealed and aged using recommended heat treatments. The materials were then isothermally exposed at 1100°F (593°C) for times up to 10,000 hours. After every 1000 hours of exposure, specimens were subjected to room temperature tensile (RTT) and high temperature tensile (HTT) testing. The microstructure of as-produced and exposed materials was characterized using optical microscopy, scanning electron microscopy and transmission electron microscopy. Variation in tensile properties with iso-

thermal exposure time was correlated with the microstructure. Further, exposed specimens were HTT tested in air and vacuum to evaluate the effect of test environment. For alloy 783, creep crack growth tests were carried out in the as-produced and isothermally exposed conditions to determine the effect of exposure on the crack growth. INCONEL® is a registered trademark of Inco group of companies.

10:20 AM BREAK

10:40 AM INVITED PAPER
ACCELERATED HIGH TEMPERATURE PERFORMANCE EVALUATION FOR ALLOY OPTIMIZATION AND REMAINING LIFE ASSESSMENT: *David A. Woodford*[1]; [1]Materials Performance Analysis, 1707 Garden St., Santa Barbara, CA 93101 USA

Creep strength and fracture resistance are two properties that are critical in the selection and optimization of high temperature alloys. These same properties may be progressively impaired by service exposure and are, therefore, key to the assessment of remaining life of high temperature components. In recent years, a methodology based on accelerated measurements of these properties using, respectively, a self-programmed variable stress creep test (stress relaxation test), and a constant displacement rate notched tensile test, has been developed. The methodology, referred to as Design for Performance, decouples these two properties. Changes in creep strength due to thermal exposure are determined principally by microstructural evolution, whereas changes in fracture resistance may be dominated by environmental interactions. Examples of the approach applied to alloy optimization and to component remaining life prediction are drawn from ferritic steels, and wrought and cast nickel based alloys, including monocrystals.

11:10 AM INVITED PAPER
CALCULATED PHASE EQUILIBRIA AND ITS USE IN PREDICTING LONG THERMAL STABILITY: *Nigel Saunders*[1]; [1]Thermotech, Ltd., Surrey Technology Centre, The Surrey Research Park, Guildford, Surrey GU2 5YG UK

Knowledge of the stable equilibrium state of a material is directly applicable to issues of long term thermal stability as it describes the state which the material ultimately tries to achieve. It is particularly useful in circumstances where kinetics enables equilibrium, or near equilibrium, to be reached. The CALPHAD route provides an excellent method by which phase equilibria can be predicted in complex alloys (ref.1). Using this approach it is then further possible to predict critical temperatures and driving forces for various transformations which can be used in kinetic equations so that rates of transformations can be predicted (ref.1). The present paper describes the current state of the art in predicting phase equilibria via the CALPHAD method for a number of material types, including Fe- and Ni-based alloys, and gives examples of its use in the area of long term thermal stability. Reference 1. N. Saunders and A. P. Miodownik, "CALPHAD - A Comprehensive Guide", Elsevier, Science, N.Y., 1998

11:40 AM
THE EFFECT OF LONG-TERM THERMAL EXPOSURE ON THE MECHANICAL PROPERTIES OF FOUR MODERN HIGH-TEMPERATURE NICKEL-BASE ALLOYS: *R. Rodger Seeley*[1]; S. Krishna Srivastava[1]; [1]Haynes International, Inc., Eng. & Tech., 1020 West Park Ave., P.O. Box 9013, Kokomo, IN 46904-9013 USA

The effect of long-term thermal exposures on the mechanical properties and microstructures of four modern nickel-base superalloys have been studied. The HAYNES® 230®, HR-120®, 556™, and 242® alloys were exposed at temperatures up to 980ϒC for times up to 20,000 hoours. The mechanical properties evaluated are tensile strength, ductility, Charpy V-notch impact energy and elastic-plastic fracture toughness. The microstructures and fracture characteristics of the materials are discussed. Long-term thermal exposures generally resulted in higher strength and lower ductility at room temperature. Fatigue at room temperature and moderately high temperatures is also effected. Low toughness values were accompanied by intergranular fracture characteristics as determined by optical and scanning electron microscopy. The fracture toughness of this material appears to be closely related to the ductility. Even for the severest exposure conditions, most high-temperature alloys still retain useable toughness.

MANUFACTURING ISSUES IN RAPID THERMAL PROCESSING: Session I

Sponsored by: Electronic, Magnetic and Photonic Materials Division, Thin Films and Interfocus Committee
Program Organizers: N.M. Ravindra, New Jersey Institution of Technology, Dept. of Phys., Newark, NJ 07102 USA; Daniel F. Downey, Varian Ion-Implant System, Gloucester, MA 01930 USA; Anthony T. Fiory, Lucent Technologies, Bell Labs., Room 1D468, Murray Hill, NJ 07974-0636 USA; Steven D. Marcus, AST Elektronik USA Inc., Tempe, AZ 85284 USA; B. Sopori, National Renewable Energy Laboratory, 1617 Cole Blvd., Golden, CO 80401 USA

Wednesday AM Room: 14A
March 3, 1999 Location: Convention Center

Session Chair: Bhushan L. Sopori, National Renewable Energy Laboratory, Golden, CO 80401 USA

8:30 AM INVITED PAPER
ULTRA-SHALLOW JUNCTION FORMATION BY RAPID THERMAL ANNEALING OF ION-IMPLANTED DOPANTS: *Aditya Agarwal*[1]; [1]Eaton Semiconductor Equipment Operations, 55 Cherry Hill Dr., Beverly, MA 01915 USA

This paper reviews recent progress in the understanding of dopant diffusion and activation, and discusses emerging strategies for formation of the extremely shallow, low-resistivity junctions required for future CMOS IC device technology generations. Shallow junction formation requires an integrated process consisting of ion implantation(I/I) and rapid thermal annealing (RTA). Process optimization therefore requires the contribution of the III and RTA parameters to be understood both separately and together. A short list of these junction formation process parameters includes: I/I -dopant species, energy and dose, as well as preamorphization implant parameters (if any); RTA-ramp-up rate, temperature control and uniformity, time and ambient. The interdependence of these parameters is exhibited by enhanced diffusion phenomena such as transient- and boron-enhanced diffusion (TED and BED). Other examples of the interdependence of the junction formation process parameters include the tradeoff between implant dose and annealing temperature, and the role of preamorphization in increasing dopant activation. These phenomena will be illustrated with experimental data. A RTA strategy, which has emerged in the last couple of years, is spike annealing, characterized by very high ramp-rates and soak times of the order of only tens of milliseconds. Spike anneals are capable of further reducing sheet resistance by allowing higher temperature anneals while limiting the overall thermal budget for diffusion. Experimental data from several sources will be compared. While the primary method for achieving ultra-shallow junctions in the foreseeable future (down to 0.13 micron technology node) appears to be RTA of ultra low energy implanted dopants, much progress has recently been made with alternative technologies such as dopant introduction by plasma immersion ion implantation (Pill), or dopant activation by laser thermal processing (LTP). The progress and limitations of these technologies will be discussed.

9:00 AM INVITED PAPER
EFFECTS OF "FAST" RAPID THERMAL ANNEALS ON SUB-KEV BORON AND BF_2 ION IMPLANTS: *Daniel F. Downey*[1]; Judy W. Chow[1]; Adam F. Bertuch[1]; Steven D. Marcus[2]; [1]Varion Ion Implant Systems, Gloucester, MA 01930 USA; [2]STEAG AST Elektronik Inc., Tempe, AZ 85284 USA

The effects of "fast" ramp-rates and spike anneals are investigated for 0.25, 0.5 and 1.0 keV "B" and for 1.1 and 2.2. keV BF_2. Below an implant energy threshold where no extended defects occur, fast ramp-rates become important in minimizing the thermal diffusion component and reducing the junction depth. Above this implant energy threshold, TED minimizes the advantages of these fast ramp-rates. Annealing

in a low and controlled 02 ppm in N_2 ambient further reduces diffusion by inimizing/eliminating oxygen related enhanced diffusion effects, while simultaneously optimizing anneal reproducibility and across-the-wafer uniformity. This paper identifies these implant and anneal conditions/ thresholds where diffusion is solely governed by thermal diffusion; and demonstrates how fast ramp-rates and spike anneals can be implemented to minimize diffusion in a controlled, reproducible and uniform 200 mm wafer process.

9:30 AM

THERMAL ACTIVATION OF SHALLOW BORON IMPLANTS: *A. T. Fiory*[1]; K. K. Bourdelle[2]; [1]Bell Laboratories, Lucent Technologies Inc, Murray Hill, NJ 07974 USA; [2]Bell Laboratories, Lucent Technologies, Inc., Orlando, FL 32819 USA

Boron implanted into n-type Si with dose in the 10^{15} cm^{-2} range and with energies from 500 eV to 5 keV was activated by annealing in nominally pure N2 and in N2 with small admixtures of 02. Various temperature-vs-time heating cycles were examined. The lowest thermal budget used heating rates up to 150ϒC/sec, cooling rates up to 800°C/sec, and minimal dwell time at the maximum temperature. Dopant activation was characterized by sheet electrical measurements. Surface oxidation was characterized by film thickness ellipsometry. Defined p-n junction depths were inferred from analysis of electrical measurements and secondary ion mass spectroscopy profiles. Fractions of activated dopant increase with boron diffusion from the implanted region, Surface oxide serves to retard dopant loss to the ambient for high-temperature anneals.

9:50 AM INVITED PAPER

SECONDARY DEFECT PROFILE RELATED TO LOW ENERGY IMPLANTED BORON MEASURED UP TO 3.5 UM DEPTH INTO Si-SUBSTRATES: *L. Soliman*[1]; M. Benzohra[2]; P. Martin[1]; K. Katata[1]; F. Boussaid[1]; A. Martinez[3]; M. Ketata[1]; [1]LEMI, Universite de Rouen, 76821 Monti-Saint-Aigman Cedex France; [2]LAAS-CNRS, 7 AV, Colonel Roche, Toulouse Cedex 310077 France; [3]INSA, Complexe Scientifique de Rangueil, Cedex 31400 France

Low energy implantation is the most promising option for ultra shallow junction formation in the next generation of silicon BICMOS technology. Among the dopants that have to be implanted, boron is the most problematic because of its low stopping, power and its tendency to undergo transient enhanced diffusion and clustering during thermal activation. This paper reports an experimental contribution with the help of secondary defect profiles to our understanding of low energy B implants in crystalline silicon. Shallow p^+n junctions were formed by low energy B Implantation 10^{15} cm^{-2} at 3 keV - into a reference or preamorphized with germanium - 10^{15} cm^{-2} at 30 KeV - n-type crystalline silicon. Rapid Thermal Annealing (RTA) for 15 sec at 950ϒC was then used. Secondary defect profiles induced by this process are measured with isothermal transient capacitance in association with Deep Level Transient Spectroscopy (DLTS). Relatively high concentrations of electrically active defects have been obtained up to 3.5 um into the crystalline silicon bulk. The relation of these defects with boron is discussed. The result is in agreement with boron transient enhanced diffusion in Si-substrate as E.J.H. Collart has reported it with back samples S.I.M.S. measurements.

10:20 AM BREAK

10:40 AM INVITED PAPER

ULTRA SHALLOW JUNCTION FORMATION OF SOURCE/ DRAIN EXTENSIONS FOR 100 NM TO 180 NM TECHNOLOGIES: A PRODUCTION WORTHY PROCESS: *Steven D. Marcus*[1]; Daniel F. Downey[2]; Wilftied Lerch[3]; Judy W. Chow[2]; Adam F. Bertuch[2]; [1]STEAG AST Elektronik, Tempe, AZ 85294 USA; [2]STEAG AST Elektronik, Gambh, Dorristadt Germany; [3]Varian Ion Implant Systmes, Gloucester, MA 01930 USA

The successful formation of S/D extensions that satisfy the National Technology Roadmap for Semiconductors (NTRS) for sub 180nm technologies has been previously reported. However, to successfully implement this process into production, precise and repeatable control of a number of variables is paramount. The substrate; the low energy implant process; the RTA temperature, temperature overshoot, anneal time, uniformity and ambient control all must be taken into consideration. The repeatability of 0.25 to 1 keV B^{11} 1.1 to 2.2 keV BF_2 and 0.5 to 2 keV As+ implants to a dose of le15/cm^2 using the Varian VIISta-80 and VIISion-80 PLUS will be demonstrated. The STEAG AST Elektronik AST3OOO rapid thermal processor will be used to demonstrate the post implant anneal repeatability. Ramp up and ramp down rates, spike vs. l0s dwell times and oxygen concentrations have the most influence on the final junction parameters. Repeatability of<1% 1sigma will be demonstrated for average Rs, junction depth and machine specific parameters for 50 and 250ϒC/s ramp up rates in conjunction with either .l0s or spike (0s) anneals. 1000ϒC (l0s) and 1050ϒC (0s) anneals will be used to gauge the performance.

11:10 AM

INFLUENCE OF VAPOR PHASE CLEANING AND RAPID THERMAL OXIDATION AND NITRIDATION ON THE SILICON - SILCONDIOXIDE INTERLACE: *N. Sacher*[1]; B. Froeschle[1]; F. Glowacki[1]; [1]STEAG AST Elektronik, Gambh, Daimierstrasse 10, Dornstadt D-89160 Germany

For 0.18 UM technology and beyond the properties of the Si/SiO_2 interface becomes more and more important Therefore a Vapor Phase Cleaning Module (VPC) is integrated in a gate Oxide Cluster Tool to ensure a good quality of the interface. As pre-oxidation cleaning different types of vapor phase cleaning (VPC) are performed in an STEAG AST Vapor Phase Cleaning Module and compared to standard wet cleaning. The oxidation, performed in a STEAG AST RTP Module, was carried out in pure oxygen 0_2 or in nitric oxide (NO). Also some oxides has been nitrided by a NO-anneal, which follows directly the oxidation. The nitrogen incorporation is investigated using Secondary Ion Mass Spectroscopy (SIMS). The roughness after the cleaning is analyzed by Atomic Force Microscopy.

11:30 AM INVITED PAPER

THIN SiO_2 FILMS GROWN FOR BRIEF OXIDATION TIMES: *A. T. Fiory*[1]; [1]Bell Laboratories, Lucent Technologies, Inc., Murray Hill, NJ 07974 USA

Bulk p -type wafers prepared with HF and RCA cleaning were oxidized in an atmospheric pressure 0_2 ambient in an incandescent-lamp processor. Minimal effective oxidation times of several seconds were obtained by rapidly heating wafers at rates up to 150ϒC/sec and then turning off lamp power just as the desired peak temperature is approached. Cooling rates vary up to about 80ϒC/sec. Films thicknesses obtained by this method increase from about 16 A for peak temperature of 1000ϒC to about 22 A for peak temperature of 1100ϒC. Oxidation process uniformity under 1% at one standard deviation over 1 5Oum wafers, equivalent to 2.5ϒC temperature variation, was obtained by optimizing relative power ratios to the lamps.

MATERIALS PROCESSING FUNDAMENTALS: Synthesis & Processing

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

Wednesday AM Room: 5A
March 3, 1999 Location: Convention Center

Session Chairs: Huimin Liu, UES Software, Inc., Annapolis, MD 21401 USA; Samim Anghaie, University of Florida, INSPI, Gainesville, FL 32611-6502 USA

8:30 AM

ELECTRICALLY POWERED PROCESSING OF NiCrAlY ALLOY POWDER: *J. M. Doh*[1]; S. K. Hur[2]; J. R. Groza[3]; [1]Korea Institue of Science and Technology, Division of Metals, P.O. Box 131, Cheongryang, Seoul 130-773 Korea; [2]Changwon National University, Dept. of Industrial Engineering, Changwon, 641-773 Korea; [3]University of California at Davis, Chemical Engineering & Materials Science Dept., Davis, CA 95616 USA

In the last decades, numerous field assisted sintering processes have been developed. Common to all these processes are particles surface phenomena related either to the electrical breakdown of surface oxides or local melting of dielectric oxide films with higher resistance. Among them, field activated sintering technique (FAST) has been recognized as very efficient in providing a quick densification. This process involves an intensive electrical discharge pulse at modest mechanical pressure application associated with resistive heating of the powder compact. Compared with other field assisted sintering processes, this process may benefit from a cleaning step due to the discharge pulse application. It is assumed that the gas molecules adsorbed on the particle surfaces and surface oxides are removed through ionization or excitation. However, the specific effect of the pulsed current application is largely unknown. The purpose of the present work is to examine the sintering characteristics of NiCrAlY and to investigate field effects on powder surface chemistry and microstructure of NiCrAlY under air, vacuum, and nitrogen atmosphere when the pulsed current (alternative current) is used for the densification of NiCrAlY powders.

8:55 AM

CaCO3 AS A SOURCE OF CALCIUM FOR ELECTROCHEMICAL SYNTHESIS OF Pb-Ca ALLOYS: Derek J. Fray[1]; *Evguenia B. Freidina*[1]; [1]University of Cambridge, Materials Science and Metallurgy, Pembroke St., Cambridge, Cambridgeshire CB2 3QZ UK

We have investigated a new electrochemical process for preparing lead-calcium alloys. Calcium metal, reduced from a molten chloride mixture, forms an alloy with liquid lead cathode. The addition of calcium carbonate to conventional CaCl2-NaCl electrolyte enables us to avoid chlorine production on the anode and replace it with oxygen and carbon dioxide. Study of the ternary system CaCl2-NaCl-CaCO3 has shown a range of melt compositions, where the electrolysis can be held below 650Ỿ. In order to prevent the side reaction of carbon deposition CO3(2-) + 4e(-)=C(s) + 3O(2-) on the cathode we have separated the anolyte from the catholyte with alumina diaphragm. The factors, which affect the level of impurities and the current efficiency of the process, are discussed.

9:20 AM

REDUCTION OF SULFUR DIOXIDE BY CALCIUM SULFIDE TO PRODUCE 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 recovery of elemental sulfur from sulfur dioxide has important implications for coal-burning power plants and nonferrous metal smelters. The thermodynamic analyses showed calcium sulfide to be suitable for recovering elemental sulfur from sulfur dioxide. At the temperatures of 973 to 1153K under the sulfur dioxide partial pressures of 5~60 kpa elemental sulfur from sulfur dioxide was recovered by calcium sulfide. The kinetics of this reaction were measured at the same conditions using a thermogravimetric analysis technique in the absence and presence of vanadium catalyst. The reactivity of regenerated calcium sulfide was also investigated. At 1073K under the sulfur dioxide partial pressure of 25.8 kpa, 50% of the original calcium sulfide in the absence, and 60% in the presence, of the vanadium catalyst was converted to calcium sulfate in an hour. The effect of the vanadium was lower in the regenerated calcium sulfide. At 1073K under the sulfur dioxide partial pressure of 25.8 kpa in the absence of the van adium catalyst, 55% of the regenerated calcium sulfide were converted to calcium sulfate in an hour even after three cycles. A "pore blocking" model was found to fit the reaction rate reasonably well.

9:45 AM

HIGH TEMPERATURE INTERACTIONS BETWEEN SILICON NITRIDE AND TITANIUM CARBIDE: *Hurman Rauf Eric*[1]; Nedret Can[2]; [1]Delft University of Technology, Faculty of Applied Earth Sciences, Mijnbouwstraat 120, Delft 2628 RX The Netherlands; [2]University of the Witwatersrand, School of Process and Materials Engineering, Private Bag 3, Johannesburg, Gauteng WITS 2050 South Africa

Kinetics and mechanism of the chemical interactions between silicon nitride and titanium carbide were investigated by isothermally reacting samples under nitrogen and argon atmospheres at temperatures between 1600//068 and 1700°C. The powder compact initially contained 20, 30, and 40 volume per cent TiC. Kinetic analyses were performed by measuring weight losses and determining the composition of titanium carbonitride ($TiC_{1-x}N_x$) at predetermined time intervals. It was found that the degree and rate of reactions increased with increasing temperature and TiC content under both nitrogen and argon atmospheres. Silicon nitride in the presence of TiC was stable under nitrogen atmosphere and the reactions were confined to silicon nitride-TiC and TiC-gas(nitrogen) interfaces. At both interfaces reactions occur by simultaneous atomic diffusion of nitrogen towards the center of the particle and desorption of carbon in the opposite direction resulting in formation of titanium carbonitrides of varying compositions. The desorbed carbon diffuses to particle surface and reacts with silicon nitride and forms SiC. This reaction proceeds by the formation of an intermediate layer of liquid silicon. Reaction products under nitrogen were β-SiC, titanium carbonitride and nitrogen gas. The maximum value of "x" in the titanium carbide formula was found to be 0.67. Silicon nitride was unstable under argon atmosphere in the presence of TiC and dissociated completely into liquid Si and nitrogen within approximately four hours of reaction time, depending upon temperature. The reaction mechanism at the initial stages under argon atmosphere is similar to the one under nitrogen. However, considerable amount of silicon nitride dissociates within the first half hour. Liquid Si aggressively attacks both titanium carbonitride and partially reacted TiC particles through cracks and pores and diffuses into the interior parts of the particle forming liquid solutions. After this stage, reactions under argon atmosphere proceeds as can be predicted from the ternary Si-Ti-C system.

10:10 AM BREAK

10:20 AM

PROCESSING AND TESTING OF PSEUDO-TERNARY CARBIDE FUELS FOR HIGH TEMPERATURE SPACE NUCLEAR REACTORS: *Travis Warren Knight*[1]; Samim Anghaie[1]; [1]University of Florida, INSPI, P.O. Box 116502, Gainesville, FL 32611-6502 USA

The development of various processing techniques for pseudo-ternary carbide nuclear fuels—namely (U, Zr, Nb)C and (U, Zr, Ta) C—is presented. Pseudo-ternary carbide samples of low uranium content

(<1g/cm3) have been investigated for the their improved thermochemical stability for application in high temperature space nuclear reactors and propulsion systems. The high melting points of pseudo-ternary carbide fuels (typically >3200K) provide for a higher service temperature and a greater specific impulse (Isp) than previous nuclear thermal propulsion designs. Techniques have been developed for the processing of pseudo-ternary carbides with efforts directed toward the development of net-shape fabrication of fuel elements. Preliminary results show that these processing techniques could be used in the fabrication of new, innovative core designs such as the square lattice or "honeycomb" design. The paper discusses the development of processing techniques for pseudo-ternary carbides and plans for hot hydrogen testing and the development of net-shape processing of pseudo-ternary carbide fuel elements.

10:45 AM

SYNTHESIS OF STABILIZED POTASSIUM FERRATE AND ITS APPLICATION IN WATER TREATMENT: *N. Neveux*[1]; N. Kanari[1]; N. Aubertin[1]; O. Evrard[1]; [1]LEM, Associated to CNRS UMR 7569, Mineral Processing and Environmental Engineering, ENSG, INPL, Vandceuvre BP 40, 54501 France;[2]Universite Henri Poincare Nancy I, Laboratoire de chimie du solide Minerale, Associated to CNRS UMR 7555, Vandceuvre BP 40, 54501 France

For the first time, dehydrated ferrous sulfate was successfully used for the diy synthesis of potassium ferrate. Moreover, ferrate ion is stabilized as a solid solution where hexavalent iron is partially substituted by S^{VI} leading to a sulfato-ferrate having the following formula K2(Fe,S)04. This substance has an efficient life time of about six months. Ferrate ion is a powerful oxidant (F^{o} = 2.2 V), a bactericidal agent and possesses coagulant, flocculant properties. Its reduction generates nascent oxygen, hydroxyl groups and $Fe(OH)_3$. Alkali metal ferrate is probably the future global agent for water treatment. Applications of this material in the field of urban and industrial effluents' treatment have been investigated. Heavy metals' removal of cations such as Ag, Cu, Cd, Mn, Ni, Pb, Zn, was successful. Results of sulfato-ferrate use for cyanide's destruction, decrease of COD, soil remediation, discoloration of pulp and paper effluents will be summarized.

11:10 AM

SYNTHESIS OF AL_2O_3-WC COMPOSITE POWDER FOR CUTTING TOOLS BY SHS PROCESS: *J. Zhang*[1]; J. J. Lee[1]; C. W. Won[1]; S. S. Cho[1]; B. S. Chun[1]; [1]Chungnam National University, Rapidly Solidified Materials Research Center (RASOM), Taejon 305-764 Korea

Al_20_3.WC Composite powder for cutting tools was synthesized by self-propagating high-temperature synthesis using Al powder as a reducing agent. WC, W2C, and A203 were concurrently formed in WO3-Al-C system. It was found that the complete reaction was achieved with excessive addition of carbon and appropriate processing parameters such as degree of dilution, particle size of aluminum, compaction pressure of green pellets and carbon source. The final product which was leached by 50% HNO3/HF diluted solution was consisted of M203-55 wt% WC having 2-3um of mean particle size.

11:35 AM

PREPARATION OF HIGH PURITY Si POWDER FOR ELECTRONIC DEVICE BY SHS PROCESS: *J. H. Lee*[1]; [1]Chungnam National University, Rapidly Solidfied Materials Research Center (RASOM), Taejon 305-764 Korea

High-purity Si powder for electronic devices especially raw material for wafer was prepared by the self-propagating high-temperature synthesis from a mixture of SiO_2 and Mg. The MgO in the product was leached with dilute HCl solution. The complete reduction of SiO_2 required excess magnesium than the stoichiometric mole ratio. The product silicon had a purity of 99.988% which was higher than that of the reactant SiO_2. This is because the impurities were either volatilized at the high temperature generated during the rapid exothermic reaction or dissolved into the HC1 solution during leaching.

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

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

Wednesday AM Room: 14B
March 3, 1999 Location: Convention Center

Session Chairs: Vijay Gupta, UCLA, Dept. of Mech. & Aero. Eng., Los Angeles, CA 90095-1597 USA; Sia Nemat-Nasser, UCSD, Center of Excellence for Adv. Mat., San Diego, CA 92093-0416 USA

8:30 AM INVITED PAPER

STRUCTURE AND PROPERTIES OF METAL/CERAMIC INTERFACES: *Manfred Ruhle*[1]; [1]Max-Planck-Institut fur Metallforschung, Seestr. 92, Stuggart D-70174 Germany

Properties of metal/ceramic interfaces determine the properties of bulk composites which are made of different constituents. Therefore, it is crucial to understand the correlation between structure and properties of those interfaces. Model studies were performed for diffusion-bonded materials where two single crystalline specimens were bonded. The atomic structure of the interface can best be revealed by transmission electron microscopy (TEM) techniques. The chemical composition of the interface and the regions near the interface can be determined by analytical electron microscopy (AEM) techniques. Information on bonding across the interface can be obtained by studies of the energy-loss near-edge structure. Mechanical four-point bending tests were done. The fracture energy is determined as a function of the diffusion-bonding conditions, different orientations and chemical composition at the interface. Results for Nb/Al2O3 and Cu/Al2O3 will be reported and compared with models existing in the literature.

9:00 AM

NANO-SCALED INTERFACIAL DEBONDING IN MULTILAYED ALUMINUM OXIDE/GOLD MATERIALS (EXPERIMENT AND THEORY): *Scott X. Mao*[1]; [1]The University of Calgary, Dept. of Mech. Eng., 2500 University Dr. NW, Calgary, Alberta T2N 1N4 Canada

To understand the interfacial cracking in thin ceramic/metal layered material is key important in the thin film and coating technology. Insitu observation on interface crack growth of microlayered aluminum oxide/gold material has been carried out. It has been found that voids exist along the interface and act as debond sources for interfacial cracking. When main crack front approaching these interfacial voids, high peak stress generated by the constrained metal layer in the front of the main crack is then acting on the voids and debonds occur. From the observation on the debonds surface by atomic force microscope AFM, we found that the debonds propagate by dislocation slip steps. The width of each slip step is 1 micro meter and height is ~10 nano meters. Based on the AFM observation, a super dislocation model in metal/ceramic layered material has been proposed to describe the crack tip stress, strain energy release rate. The crack tip blunting and toughening due to dislocation shielding from interface crack has been analyzed. The meal length scale (thickness) effect on the interfacial cracking and toughening has been found.

9:20 AM INVITED PAPER

SCRATCH OF POLYMER COATINGS WHICH ADHERES TO THE INDENTER: *James C. M. Li*[1]; [1]University of Rochester, Materials Science, College of Arts, Sciences and Eng., Rochester, NY 14627 USA

The load displacement relations for a spherical indenter which adheres to a film coating over a substrate is studied including the area of contact as a function of the normal load, film thickness and the interfacial energy between the film and the indenter. This indenter is then used to scratch such a film coating so that the relation between the horizontal force required as a function of normal load and the scratching speed can be understood. In the elastic or anelastic region, there are no scratch marks left afterwards. But when the normal load exceeds a critical value, the film is damaged with a possible de-adhesion of the film from its substrate. Since the scratch test is thermodynamically unstable, it bifurcates into stick/slip stages which will be described. Work supported by NSF through DMR 9623808 monitored by Dr. Bruce MacDonald. An Industrial Fellowship award from Eastman Kodak Company and the NSF Institute for Mechanics and Materials directed by Marc Meyers is gratefully acknowledged also.

9:50 AM

QUANTITATIVE CHARACTERIZATION OF SCRATCH AND MAR BEHAVIOR OF POLYMERIC COATING SURFACES: *Li Lin*[1]; Gregory S. Blackman[2]; Robert R. Matheson[1]; [1]Dupont Company, Marshall R&D Laboratory, 3401 Grays Ferry Ave, Philadelphia, PA 19146 USA; [2]Dupont Company, CR&D, Experimental Station, E323-110B, Wilmington, DE 19880 USA

Scratch and mar damage of automotive topcoats is of increasing concern to the automobile industry and its customers. To better characterize and understand scratch and mar behavior, we developed a microscratch technique which measures normal and tangential force with a few micronewtons precision, and penetration depth with a few nanometers precision as function of time or position during a scratch experiment. With this technique, scratch and mar resistance is evaluated based on plastic and fracture thresholds. This technique allowed us to prepare well defined scratches in terms of damage type (plastic or fracture) and size. A statistic survey was conducted relating these damages to visual appearance. In addition, loading rate, scratch rate, aging and other parameters that may effect scratch and mar resistance of polymer coatings were also examined.

10:10 AM BREAK

10:20 AM INVITED PAPER

MEASUREMENT OF THE INTERFACE CRACK VELOCITY AND THE BRITTLE-TO-DUCTILE TRANSITION TEMPERATURE : *Vijay Gupta*[1]; Michael O'Brien[1]; Jianxin Wu[1]; [1]University of California, Dept. of Mechanical and Aerospace Engineering, 38-137E, Engg. IV Bldg., Los Angeles, CA 90095-1597 USA

A technique to measure the interface crack velocity has been developed with a view to study the brittle-to-ductile transition phenomenon in bimaterial interface systems involving metallic coatings. The experimental strategy involved generating a line crack of approximately 100 μ/m in extent at an interface between a 1 μ/m-thick and 600 μ/m wide Nb strip and a (0001) surface of sapphire, using photolithography. A microcircuitry consisting of equi-spaced Al wires of 100 A thickness was deposited orthogonally on top of the Nb strip, including the areas beyond the crack tips. A compressive stress wave of approximately 20 ns duration was generated on the backside of the sapphire substrate by exfoliating a constrained Al film by a Nd:YAG laser pulse. The compressive stress wave upon reflecting into a tensile wave from the free surface of the coating led to the initiation of the interface crack. The critical stress pulse amplitude was obtained by recording the transient velocity of the sapphire's free surface, away from the crack tip region, by using an optical interferometer. Prior to wave loading, a small current was introduced in the Al wire mesh to establish a circuit such that the voltage drop across the reference resistor was proportional to the number of Al lines broken by the propagating crack front. Because the voltage-change occur rather quickly, it was impossible only to record changes proportional to this voltage on a fast digitizer with a 5 ps rise-time. Thus, the recorded voltage-time record provided information only on the total duration of crack propagation. An independent measure of this parameter was also obtained by recording free surface velocity of the sapphire by an interferometer. To compute average crack velocity, the total crack advance during this time was obtained by viewing the shock-loaded specimens under a scanning electron microscope. The measured critical free surface velocity at crack initiation was used to calculate the energy flow at the crack tip (equal to the interface toughness) by using a simulation based on dynamic fracture. Thus, the present setup allows the measurements of both the interface crack velocity and the interface toughness. At ambient temperature, the interface crack velocity was found to approach the Raleigh wave speed of the stiffer material, which challenges all the presently available models of dynamic fracture as the energy release rate becomes zero at the measured crack speeds. The above apparatus is being used to measure the interface crack speeds and toughness as a function of temperature. This should lead to the determination of the brittle-to-ductile transition temperature, beside providing a means to understand the local inelastic processes that contribute to the plastic component of the measured interface toughness.

10:50 AM

MICROMECHANICS OF COMPRESSION FAILURE OF FIBER-REINFORCED COMPOSITES: *Jeffrey D. McGee*[1]; Sia Nemat-Nasser[1]; [1]University of California, San Diego, Center of Excellence for Advanced Material, 9500 Gilman Dr., San Diego, CA 92093-0416 USA

Micromechanics-based modeling of failure mechanisms in heterogeneous and anisotropic composites is considered, focusing on the phenomenon of kink-band formation in woven composites under biaxial compressive dynamic loads. Using a modified split-Hopkinson bar, samples of woven fiber-reinforced polymeric composites are subjected to biaxial compression, and the process of initiation and growth of kink bands is captured by high-speed photography. A micromechanics model is developed to describe this phenomenon by homogenizing a periodic composite with woven fibers into a homogenous but anisotropic effective material and then examining the process of growth of an array of interacting wing cracks within the effective anisotropic solid. The resulting properties' degradation and the failure mechanisms are studied.

11:10 AM

INFLUENCE OF FIBER COATING THICKNESS ON FRACTURE BEHAVIOR OF CONTINUOUS WOVEN NiCaLoN® FABRIC-REINFORCED SILICON-CARBIDE MATRIX CERAMIC COMPOSITES: James H. Miller[1]; Rick A Lowden[1]; *Peter K. Liaw*[2]; John D. Landes[3]; [1]Oak Ridge National Laboratory, P.O. Box 6423, Oak Ridge, TN 37831-6423 USA; [2]University of Tennessee, Materials Science and Engineering, 427B Dougherty Building, Knoxville, TN 37996-2200 USA; [3]University of Tennessee, Mechanical and Aerospace Engineering and Engineering Science, Perkins Hall, Knoxville, TN 37996 USA

Nicalon® plain-weave fiber fabric-reinforced silicon carbide (SiC) matrix composites with various pyrolytic carbon fiber/matrix interface coating thicknesses have been successfully fabricated by forced chemical vapor infiltration (FCVI) methods. The influence of the carbon interface coating thickness on the fracture behavior of these fiber fabric-reinforced SiC composites has been investigated. Experimental results indicate that fiber coating thickness significantly alters the fracture behavior of SiC composites. The fracture strength exhibits a maximum as the coating thickness increases. A theoretical model has been developed to simulate the fracture behavior in the SiC composites with varied carbon interface coatings. The model assumes that microcracking, which is due to low matrix toughness, continuously initiates and arrests. The model-predicted fracture behavior compares well with the experimental results. This research was performed in cooperation with the University of Tennessee, Knoxville, under contract 11X-SN191V with Lockheed-Martin Energy Research Corporation and is sponsored by the US Department of Energy, Assistant Secretary for Conservation and Renewable Energy, Office of Industrial Technology, Industrial Energy Division, under contract DE-AC05-84OR21400 with Lockheed Martin Energy Research Corporation.

11:30 AM

DEFORMATION AND FRACTURE OF A COMPOSITE REINFORCED WITH BONE-SHAPED SHORT FIBERS: *Yuntian T. Zhu*[1]; James A. Valdez[1]; Michael G. Stout[1]; Ning Shi[2]; Shujia Zhou[3]; Darryl P.

Butt[1]; Terry C. Lowe[1]; [1]Los Alamos National Laboratory, Materials Science and Technology, MS G 755, Los Alamos, NM 87545 USA; [2]Los Alamos National Laboratory, Los Alamos Neutron Science Center, MS H805, Los Alamos, NM 87545 USA; [3]Los Alamos National Laboratory, Applied Physics Division, MS B-258, Los Alamos, NM 87545 USA

The fiber-matrix interface in short-fiber composites is a limiting factor in improving mechanical properties such as strength and toughness. A strong interface makes it difficult to relieve fiber stress concentration in front of an approaching crack, and results in fiber breakage, while a weak interface cannot effectively transfer load from matrix to fiber. We have found that bone-shaped short-fibers can overcome this problem by transferring load through the enlarged fiber ends while having a weak interface. It is also found that bone-shaped fibers can effectively bridge cracks and to stop crack propagation. This presentation will discuss the deformation and failure processes of bone-shaped-short-fiber reinforced composites, and explain why the bone-shaped short-fiber composites have both higher strength and toughness than conventional short-fiber composites.

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

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

Wednesday AM Room: 11B
March 3, 1999 Location: Convention Center

Session Chair: Harish Merchant, Gould Electronics, Eastlake, OH 44095 USA

8:30 AM INVITED PAPER
ELASTIC CONSTANTS OF METALLIC SUPERLATTICES: *Ivan K. Schuller*[1]; M. Grimsditch[2]; [1]University of California, San Diego, Physics Dept. 0319, 9500 Gilman Dr., La Jolla, CA 92093-0319 USA; [2]Argonne National Labs, Materials Science Division, Argonne, IL 60439 USA

Metallic superlattices exhibit interesting elastic anomalies which are correlated with structural changes. Many of these findings are controversial and often contradictory. These include anomalies in the shear, biaxial, flexural and Young's modulii of a variety of metal/metal, metal/semiconductor and ceramic/ceramic superlattices. We will describe a series of experiments relating mechanical anomalies with structural and electronic properties. These will then be discussed in light of theoretical models which have been proposed to explain the anomalous elastic properties.

9:10 AM INVITED PAPER
FATIGUE OF COPPER/POLYIMIDE LAMINATE, COPPER/ADHESIVE/POLYIMIDE MULTI-LAYER CONSTRUCTION AND COPPER-BASED FLEXIBLE PRINTED CIRCUIT: *Harish D. Merchant*[1]; Sidney J. Clouser[1]; Duane B. Mahnke[2]; [1]Gould Electronics, 34929 Curtis Blvd., Eastlake, OH 44095 USA; [2]Rogers Corporation, 100 N. Dobson Rd., Chandler, AZ 85224-6196 USA

Copper is bonded to the dielectric film by plasma treatment of the film surface prior to copper deposition; alternately it is bonded through an intermediate adhesive layer between the polyimide substrate and the thin copper foil. The copper is present as a continuous layer or as an etched line pattern of a given linewidth and pitch. In the flexible circuit, the copper lines are symmetrically sandwiched between the polymeric adhesive and dielectric layers. During cyclic loading, the load transfer and the strain accommodation between layers and the residual stress fields within copper dramatically alter the fatigue behavior of copper which either "rides" on the polymeric substrate or is effectively shielded from fatigue damage. The net effect is an orders of magnitude enhancement of fatigue life. The strain-based fatigue is characterized in the flex and fold modes for a wide range of strain amplitudes. Alternately, for a given strain amplitude, the flexible circuit is characterized in a roll fatigue mode whereby one side of the copper surface is subjected to tension/tension and the other side to compression/compression type loadings. If the inter-layer delamination and the variations in layer thickness are controlled, the mean fatigue life as long as 100×10^6 cycles to failure and a statistical description of fatigue are possible. The tension/compression fold fatigue mode mimics the printer hinge motion and the tension/tension plus compression/compression roll fatigue mold mimics the disk drive motion.

9:40 AM INVITED PAPER
INFLUENCE OF MICROSTRUCTURE SIZE ON THE PLASTIC DEFORMATION KINETICS, FATIGUE CRACK GROWTH RATE AND LOW-CYCLE FATIGUE OF SOLDER JOINTS: *Hans Conrad*[1]; Z. Guo[1]; Y. Fahmy[1]; Di Yang[1]; [1]North Carolina State University, Dept. of Mats. Sci. and Eng., Advanced Materials & Electro-Effects Laboratory, Raleigh, NC 27695-7907 USA

This paper reviews the work by the present authors and that in the literature on the effects of microstructure size on the plastic deformation kinetics (PDK), fatigue crack growth rate (FCGR) and low-cycle fatigue (LCF) of near eutectic Pb-Sn solder joints. Variation in microstructure size were obtained by: (a) varying the cooling rate following reflow, (b) isothermal annealing and (c) thermo-mechanical cycling (TMC). The principal microstructure features considered are the mean colony size dc and the average eutectic phase size d(Pb-Sn) = (d(Pb + dSn))/2. A decrease in the as-reflowed microstructure size had the following effects at shear stresses $t(tou)/m(mu) < 2 \times 10^{(-3)}$: (a) decreased the flow stress, (b) decreased the FCGR and (c) increased the fatigue life. Opposite behavior tended to occur for $t(tou)/m(mu) > 2 \times 10^{(3)}$. The effects of phase coarsening by isothermal annealing or TMC wore more complex, but in general tended to be similar to those for the as-reflo wed microstructure size. Constitutive equations are prepared which predict behavior in reasonable agreement with experiment.

10:10 AM BREAK

10:20 AM INVITED PAPER
MECHANICAL SPECTROSCOPY IN THE STUDY OF ANELASTIC AND STRUCTURAL BEHAVIOUR OF NANOSTRUCTURED METALS: *Ennio Bonetti*[1]; [1]Dipartimento di Fisica dell'Universita di Bologna, Gruppo Struttura Della Materia, Viale Berti Pichat 6/2, Bologna I-40127 Italy

Nanostructured (n-) metals due to their unusual specific physical properties have been the subject of a lot of theoretical and experimental investigations in recent years. A well used approach to study this class of materials refers to a simple two-components structural model consisting of the crystallites with dimensions in the nanometer range and the interfaces or interfacial phase. The high interface (surface) to volume ratio and the detailed structure of the interfaces are responsible for some of the interesting and specific properties of these materials. The Mechanical Spectroscopy approach to study the mechanical properties in the anelastic and or viscoelastic regime of n-metals demonstrated to be a powerful structure sensitive probe up to now not yet extensively employed, detailed information on some specific parameters determining the mechanical behaviour and the structural stability of n-materials can be obtained through measurements of the real and imaginary components of the complex mechanical susceptibility. These include the short range interfaces dynamics, whether it is of relaxational or viscoelastic-nature as well as the occurrence of structural relaxation and or

phase transitions affecting the interfaces without appreciable grain growth. These last effects are driven by microstrain localization at the interfaces occurring when entering the nanometer regime. Some examples and recent results dealing with mechanical spectroscopy measurements on nanostructured Al and Ni will be presented. The anelastic behaviour of these materials will be discussed with particular reference to structural stability against grain growth relaxation mechanisms at the interfaces and mechanical behaviour at high homologous temperatures.

10:50 AM INVITED PAPER

CYCLIC DEFORMATION BEHAVIOUR OF ULTRAFINE GRAIN COPPER: *Sean R. Agnew*[1]; A. Yu Vinogradov[2]; J. R. Weertman[1]; R. Z. Valiev[3]; [1]Northwestern University, Evanston, IL 60208 USA; [2]Kanazawa University, Kanazawa 920 Japan; [3]Ufa State Aviation University, Ufa Russia

The metals processed by severe plastic deformation techniques have come to be known as ultrafine grain (UFG) or submicrocrystalline metals and have received much interest recently. One area of study that has produced contradictory results is fatigue performance, namely whether or not UFG Cu undergoes fatigue softening. Recently, through careful TEM observation, continued fatigue testing, and differential scanning calorimetry new answers have been obtained to explain previous contradictions. We can now present a clearer picture of UFG Cu's fatigue performance. A summary of the investigation including Coffin-Manson and S-N plots, static recrystallization kinetics, and failure behavior will be presented.

NANOSTRUCTURED HYBRID MATERIALS: Synthesis and Processing

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 Phy., 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

Wednesday AM Room: 16A
March 3, 1999 Location: Convention Center

Session Chair: Robert D. Shull, NIST, Dept. of Magnetic Mats., Gaithersburg, MD 20899 USA

8:30 AM INVITED PAPER

NANOCHANNEL GLASS ARRAYS: *Ronald Joseph Tonucci*[1]; [1]Naval Research Laboratory, Code 5611, 4555 Overlook Ave., Washington, D.C. 20375 USA

Nanochannel glass arrays are complex glass composites with features as small as 10 nanometers. The interface between composite elements must be tightly controlled to avoid diffusion at these small lateral dimensions. By carefully controlling process conditions, 2-dimensional arrays have been fabricated with packing densities as high as 100 billion elements per square centimeter. A number of glass compositions have been used to fabricate the arrays and the composite can be engineered to contain etchable glass materials. Upon removal of the etchable glass, an array of highly regular channels can be formed. The arrays are thermally stable to temperatures in excess of 600ϒC and under certain conditions can be modified to be thermally stable to temperatures as high as 1000ϒC. A variety of materials have been deposited into the channels of the array to create high aspect ratio nanowires. Materials include metals, polymers and semiconductors with diameters as small as 33 nm. The fabrication and characterizat ion of these nanostructured hybrid materials will be discussed along with several applications.

9:00 AM

SELF-ASSEMBLED MAGNETIC NANOPARTICLE ARRAYS: *Sara A. Majetich*[1]; Yan Jin[1]; Cindi L. Dennis[1]; [1]Carnegie Mellon University, Dept. of Physics, 5000 Forbes Ave., Pittsburgh, PA 15213-3890 USA

Ordered arrays of magnetic nanoparticles are prepared by two methods: the synthesis of a nonmagnetic liquid crystals which are solidified and transformed to a ferrimagnetic iron oxide phase, and the self-assembly of monodisperse ferromagnetic cobalt particles with uniform nonmagnetic coatings. Compared to other self-assembling systems, magnetic nanoparticles have an additional magnetostatic force, which can be either attractive or repulsive. This favors the formation of magnetically aligned chains of magnetic dipoles, rather than two- or three-dimensional structures. Both of the synthetic routes overcome this problem by making the magnetic forces weak relative to other interactions during the self-assembly process. Transmission electron microscopy (TEM) is used to characterize the degree of ordering of the nanoparticle arrays. The magnetization directions of individual particles and direct evidence of interparticle coupling are obtained from the Foucault method of Lorentz microscopy. Particle interactions ar e also characterized by magnetic force microscopy (MFM), showing the transition between chain-forming and layer-forming behavior.

9:20 AM BREAK

9:50 AM INVITED PAPER

MECHANICAL PROPERTIES OF THERMAL SPRAY NANO HYBRID COATINGS: *Peter Strutt*[1]; [1]Inframat Corporation, 20 Washington Ave., Suite 106, North Haven, CT 06473 USA

A methodology has been developed to deposit nanostructured coatings of hard ceramic materials by DC plasma thermal spraying. One of these nanocoating materials is alumina-13 wt% titania, which is deposited on steel substrates using a Metco 9MB plasma-arc gun. In examining sliding wear behavior, comparative studies have been made with coatings produced using conventional Metco 130 alumina-13 wt% titania powder feed material. The studies show that the properties of deposited coatings depend on the morphology and chemical composition of the agglomerated nanoparticle feed powder. When the thermal spray fed powder consists of hollow shell agglomerated nanoparticles, the wear resistance of the coatings is only slightly better (40%) than that of coatings produced with conventional Metco 130 powder. However, using solid nanoparticle agglomerated Al2O3/TiO2 powder there is a 200% wear resistance improvement over the conventional counterpart. Interestingly, the addition of nanostructured yttria-stabilized zirconia (n-Y SZ) to the powder feed is significant, for example, a 5 wt % addition of n-YSZ results in a fourfold reduction in weight loss during sliding wear.

10:20 AM

NONEQUILIBRIUM ALLOYS AND COMPOSITES IN NANOSTRUCTURED TWO-PHASE ALLOYS: *Evan Ma*[1]; J. H. He[1]; H. W. Sheng[1]; P. J. Schilling[2]; [1]The Johns Hopkins University, Dept. of Mats. Sci. and Eng., Baltimore, MD 21218 USA; [2]Louisiana State University, Center for Advanced Microstructures and Devices, Baton Rouge, LA 70803 USA

Using the Cu-Fe system as a model system, we discuss the formation of highly nonequilibrium alloys and composites in nanophase powder mixtures prepared by mechanical milling. Even though the system exhibits positive heat of mixing and negligible solid solubility at ambient temperature in equilibrium, atomic-level alloying between Cu and Fe occurs in nanophase mixtures of Cu and Fe produced by milling, forming either a single phase supersaturated solid solution, or a two-phase microstructure comprising both fcc and bcc solution phases. Extended X-ray Absorption Fine Structure (EXAFS) and X-ray Absorption Near-Edge Structure (XANES) techniques have been used to monitor changes in local environments and determine the compositions and volume fractions of the coexisting phases. Molecular Dynamics (MD) simulations have been used to elucidate atom-level structural evolution at the interfaces between the two nanostructured constituent elements with and without the presence of plastic deformation. Based on the findings from

experiments and simulations, the alloy formation and two-phase coexistence are explained in terms of the dynamics, energetics and heterogeneity of the nonequilibrium defects and external forcing events. The alloyed nanocrystalline solid solution powders have been used as precursors to obtain uniform two-phase nanocomposites through in situ phase decomposition during hot consolidation into bulk samples. The mechanical properties of the fully dense two-phase nanocomposites obtained are explained in terms of, in addition to the effects of phase volume fractions and grain sizes, the topological arrangements of the two-phase microstructure and effectiveness of the interphase interfaces as slip transmission barriers.

10:40 AM

PROCESSING OF Ni-SiO2 NANOCOMPOSITES USING SEVERE PLASTIC TORSIONAL STRAINING: *Y. T. Zhu*[1]; I. V. Alexandrov[2]; A. V. Korznikov[2]; T. C. Lowe[1]; R. Z. Valiev[2]; [1]Los Alamos National Laboratory, Mats. Sci. and Tech. Division, MG G755, Los Alamos, NM 97545 USA; [2]Ufa State Aviation Technical University, Institute of Physics of Advanced Materials, K. Marksa 12, Ufa 450000 Russia

Severe Plastic Torsional Straining (SPTS) is a technique to induce large plastic shear deformation under high stress. It has been widely used to refine the grain size of monolithic metals and alloys, as well as to consolidate both micrometer-sized and nanometer-sized powders. This presentation will report the processing of Ni-SiO2 nanocomposites by SPTS consolidation of Ni-SiO2 powder mixtures. It is shown that the SPTS process can simultaneously consolidate the Ni-SiO2 powders and refine the grain size. The SPTS-consolidated nanocomposites is >98% dense. Microstructures, mechanical properties and thermal stability of the SPTS consolidated nanocomposites will be discussed.

11:00 AM

NANOCOMPOSITE MATERIALS PREPARED BY AEROSOL SYNTHESIS USING QUANTUM DOTS AS BUILDING BLOCKS: *J. M. Nedeljkovic*[1]; D. P. Uskokovic[1]; [1]Vinca Institute of Nuclear Science, Belgrade & Institute of Technical Sciences of the Serbian Academy of Sciences and Arts, Belgrade Yugoslavia

Spherical non-agglomerated nanocomposite particles and coatings of complex composition and controlled phase content, suitable for direct application or fabrication of high tech materials can be prepared by aerosol synthesis using ultrasonic spray pyrolysis of quantum dots as building blocks. Microscopic techniques with different level of resolution, such as scanning electron microscopy, high resolution field emission scanning electron microscopy, atomic force microscopy and scanning tunnelling microscopy were used. The methodology provides general procedure for the rational design of novel and potentially useful nanocomposite materials.

SURFACE ENGINEERING: SCIENCE AND TECHNOLOGY I: Hard Coatings

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

Wednesday AM Room: 7B
March 3, 1999 Location: Convention Center

Session Chairs: Douglas H. Lowndes, Oak Ridge National Laboratory, Solid State Div., Oak Ridge, TN 37831-6056 USA; Sun Kyu Kim, University of Ulsan, School of Mats. and Met. Eng., Mugeodong, Ulsan 680-749 Korea

8:30 AM INVITED PAPER

SURFACE DESIGN TOWARD WEAR-RESISTANT, SELF-LUBRICATING COATING: *Kazuhisa Myoshi*[1]; [1]National Aeronautics and Space Administration, Lewis Research Center, Cleveland, OH 44135 USA

High tribological reliability is of crucial importance in operating the many interacting surfaces that are in relative motion in mechanical systems. Improving the tribological functionality of materials such as achieving low friction and good wear-resistance is an aim of this investigation. According to the adhesion theory of metallic friction (mu = sA/W) and the relation between the coefficient of friction and the total surface energy in the real area of contact (mu ~ gamma.A), reducing friction requires minimizing the shear strength of the interface s, the real area of contact A, the total surface energy in the real area of contact gamma.A, and the plowing or cutting contribution (where W is the normal load). Reducing wear generally requires minimizing these factors while maximizing the hardness, strength, and toughness of bulk materials. Toward this end, surface engineering studies were used to describe several tribological coatings, including carbon-based and boron nitride coatings. Surface and bulk material properties, which determine the adhesion, friction, and wear behavior of interacting materials, are described. The primary emphasis is on the nature and character of these coatings, especially their surface chemistry, atomic bonding state, and microstructure. In addition, the reduction of friction and wear by thin oxide, carbon-based, and boron-based films that are formed on metal and ceramic surfaces is stated.

8:55 AM INVITED PAPER

CATHODIC-ARC CARBON FILMS AS PROTECTIVE OVERCOATS FOR DISK DRIVE APPLICATIONS: *W. Fong*[1]; D. Bogy[1]; C. S. Bhatia[2]; [1]University of California, Dept. of Mechanical Engineering, Berkeley, CA 94720 USA; [2]IBM SSD, 5600 Cottle Rd., San Jose, CA 95193 USA

Hydrogenated (CHx) and nitrogenated (CNx) carbon films ranging in thicknesses 7 nm and up are commonly used as protective overcoats on media found in disk drives today. However, as a real densities continue to increase, thinner overcoats (< 7 nm) will be needed to reduce the magnetic spacing between the head and disk. At these thicknesses, film properties such as surface coverage, corrosion protection, and wear durability affect the overall tribological performance of the head-disk interface. Cathodic-arc carbon films have been investigated in this paper as an alternative to CHx and CNx overcoats and results from nano-indentation tests, corrosion tests, and a series of tribological tests are summarized.

9:20 AM

CHARACTERIZATION OF TiN/CN_X MULTILAYERS DEPOSITED BY DC MAGNETRON SPUTTERING: *Y. H. Chen*[1]; [1]Northwestern University, Dept. of Materials Science and Engineering, Evanston, IL 60208 USA

Titanium nitride - carbon nitride multilayers (TiN/CNx) with TiN (111) crystalline orientation have been studied in order to obtain hard coatings with good tribological properties. Thin CNx layers were deposited to interrupt the growth of TiN in order to suppress the TiN columnar structure. The films were deposited by reactive DC magnetron sputtering on Si (100) substrates at room temperature. Deposition pressure as low as 2.5 mTorr in an argon-25% nitrogen mixture were determined to be the best deposition conditions for obtaining TiN (111) texture. Bias voltage was applied on the substrate to enhance ion bombardment of the growing film. The thickness ratio of TiN/CNx layers varies from 1 to 10 keeping CNx thickness equal to 0.75 nm. Low-angle x-ray diffraction showed good interface between layers. The internal stress measured by the substrate curvature is directly related to the layer thickness ratio, i.e., smaller thickness ratio gives smaller internal stress. The surface roughness relates to the thickness ratio in the same way. Multilayers show better tribological performance than monolithic TiN thin films.

9:35 AM

13C NMR SPECTROSCOPY OF AMORPHOUS HYDROGENATED BORON CARBIDE AND AMORPHOUS HYDROGENATED CARBON NITRIDE: *Janet Braddock-Wilking*[1]; Joseph LaManna[1]; Shu-Han Lin[1]; Bernard J. Feldman[1]; [1]University of Missouri-St. Louis, Departments of Chemistry and Physics, Center for Molecular Electronics, St. Louis, MO 63121 USA

We report the 13C NMR spectrum of amorphous hydrogenated boron carbide and amorphous hydrogenated carbon nitride. Both alloys are grown in an rf CVD plasma reactor. The amorphous hydrogenated boron carbide spectrum is dominated by one line at 15 ppm. We interpret this line as due to carbon bound in boron carbide icosahedra, because polycrystalline boron carbide with boron carbide icosahedra as the unit cell gives a very similar NMR spectrum. The amorphous hydrogenated carbon nitride spectrum consists of two broad lines centered at 20 ppm and 130 ppm and two sharp lines at 131 ppm and 164 ppm. The broad line at 130 ppm and sharp line at 131 ppm are due to sp2 carbon in an amorphous matrix and crystalline environment, respectively. The broad line at 20 ppm is possibly due to sp2 carbon bound to a nitrogen atom in an amorphous matrix. The sharp line at 164 ppm is not understood, but is probably related to the sharp 164 ppm line previously observed in the NMR spectrum of amorphous carbon nitride grown by magnetron sputtering.

9:50 AM

STUDY OF CN_X FILMS DEPOSITED BY ICP-CVD FROM N_2/CCl_4/H_2 PRECURSORS: Marie-Paule Delplancke-Ogletree[1]; *Jiri Bulir*[1]; [1]Université Libre de Bruxelles, Metallurgy - Electrochemistry, CP 165, 50 Avenue F.D. Roosevelt, Brussels 1050 Belgium

Thin CN_x films were deposited on silicon substrate by inductively coupled r.f. plasma chemical vapor deposition (ICP-CVD). Gas mixture of N_2 /CCl_4 /H_2 was used for the deposition. Influence of deposition parameters on film quality and plasma properties was studied. Nature of gaseous species, electron temperature an plasma density were obtained by optical emission spectroscopy and Langmuir probe measurements. Pressure, ratio of H_2 to CCl_4, substrate temperature and injected r.f. power were varied in the following ranges: p=10-200 Pa, H_2 /CCl_4=1-10, T_s =100-400 C, and P=50-300W. Film composition was studied by AES before and after in-situ Ar ion sputtering. The N/C ratio varied in the range of 0.5-0.7. Chlorine contamination of the deposits was detected but could be reduced by optimizing the deposition conditions. Decrease of both, Nitrogen and Chlorine concentrations was observed after the surface was sputter cleaned. Fourier transform infrared spectroscopy (FTIR) was used for determination of chemical bonding. Presence of Hydrogen was confirmed by N-H stretching vibrational band at 3350 cm^{-1} and weak C-H stretching band. A group assigned to C=C and C=N was detected around 1650 cm^{-1} as well as a nitril CN group at 2220 cm^{-1}. Surface morphology of the films was studied by atomic force microscopy (AFM).

10:05 AM

INVESTIGATION OF MECHANICAL PROPERTIES OF Ti(C,N) AND TiN THIN FILMS DEPOSITED ON CUTTING TOOLS: *Erich Lugscheider*[1]; Cyrus Barimani[1]; Markus Lake[1]; [1]Aachen University of Technology, Materials Science Institute, Aachen Germany

Increasing demands on production processes in terms of performance, reliability and environmental compatibility shape the specification profile for modern wear resistant coating systems. The cutting process is determined by a complex kind of straining. Due to this fact, the cutting tools should possess complement properties, like hardness and toughness. These complement requirements are fulfilled by PVD coated cutting tools. Especially specific cutting operations like high speed cutting (HSC) or cutting without coolants necessitate PVD coated cutting tools. The performance and tool lifetime of PVD coated cutting tools is mainly influenced by the mechanical properties like hardness, residual stress or bond strength of coating and substrate. For the present work three different substrate materials, high speed steel, cemented carbides and cermets, were coated with Ti(C,N) and TiN. The deposition processes were carried out with the Cathodic Arc Ion Plating Process by varying the layer thickness. Depending on different layer thicknesses, the mechanical properties like hardness, residual stress or bond strength were investigated. To determine the hardness a nanoindenter was used. The bond strength was investigated by the scratch test and a hardness test called Rockwell C test. To investigate the residual stress a stripe bending test was used. This paper describes the experimental techniques and the results of the mechanical film properties in consideration of different film thicknesses.

10:20 AM INVITED PAPER

OVERVIEW-HIGH DEPOSITION RATE CERAMIC-METALLIC COATINGS BY ELECTRON BEAM-PHYSICAL VAPOR DEPOSITION (EB-PVD) PROCESS: *Doug Wolf*[1]; J. Singh[1]; [1]The Pennsylvania State University, Applied Research Laboratory, State College, PA 16804 USA

Chromium, titanium carbide (TiC) and partially yttria stabilized zirconia (YSZ) coatings deposited by energy electron beam-physical vapor deposition (EB-PVD) will be presented along with their potential applications. Interest in replacing chromium electroplating process has sparked the use of EB-PVD technology for the repair of many components including landing gears due to relatively high deposition rate (100-150 m/minute with an evaporation rate ~ 10-15 Kg/hour), dense coatings, precise composition control, columnar and poly-crystalline microstructure, ad low contamination. This paper discusses the microstructure, wear behavior and friction coefficients of chromium coatings produced by EB-PVD and will be compared with thermal sprayed WC-Co coatings. In addition, the surface morphology, microstructure and texturing of TiC films produced by reactive ion beam assisted EB-PVD will be discussed for wear resistant applications including cutting tool industry. YSZ has also been grown by EB-PVD resulting in a columnar microstructure for thermal barrier applications (TBC). Microstructural evolution of various ceramic and metallic coatings developed by the EB-PVD process will be presented.

10:45 AM BREAK

11:00 AM INVITED

TRIBOCHEMICAL POLISHING OF SILICON NITRIDE AND CARBIDE: *T. E. Fischer*[1]; V. Muratov[1]; Z. Zhu[1]; [1]Stevens Institute of Technology, Hoboken NJ 07030

Tribochemical polishing is the removal of material by a chemical reaction that is stimulated by friction. Scratch-free surfaces with a roughness R_a = 0.5 nm are routinely obtained on silicon nitride. The chemical and mechanical anisotropy of silicon carbide decrease the polishing ability, resulting in surfaces with a roughness R_a = 1.2 nm. The mechanisms by which friction accelerates the chemical reaction have been studied by measuring the reaction rate as a function of temperature, reagent concentration, normal force and sliding speed. In all cases, it is found that the reaction rate is proportional to the friction coefficient above a threshold that depends on the reactive fluid. The specific temperature-dependence is small, showing that the activation energy for the reaction is reduced from 120 to less than 10 kJ/mole by friction. Two tribochemical mechanisms have been identified: the growth of a

surface layer that is removed by friction operates at low sliding speeds only and a direct stimulation of the reaction is observed in all other conditions.

11:25 AM INVITED
CURRENT ISSUES IN TOTAL HIP ARTHROPLASTY: THE HEAD-STEM INTERFACE: *Ramakrishna Venugopalan*[1]; Linda C. Lucas[1]; [1]Department of Biomedical Engineering, Univeristy of Alabama at Birmingham, 1075 13th Street South, Birmingham, AL 35294-4440

Modular connections commonly exist at the head-stem region in total hip arthroplasties (THAs) and allow for adaptation of the metaphyseal-diaphseal ômis-matchö of the anatomy. Modularity takes advantage of the material properties of the different combinations of materials specifically suited for the functional needs of the various implant components and is thus a very cost-effective solution to the difficult demands of THA. However, modularity also places increased demands on manufacturer and surgeon alike in terms of design, manufacture, and assembly issues. This talk will address specific concerns regarding electrochemical-mechanical interactions in mixed-metal modular head-stem connections in THAs. The effect of a nitrogen diffusion-hardening process on the titanium alloy component with reference to improving the resistance of the head-stem interface to electrochemical-mechanical interactions will also be presented and analyzed.

11:50 AM
APPLICATION OF ELECTRON SPECTROSCOPY FOR THE ENHANCEMENT OF METASTABLE CERAMIC FILMS: *R. Cremer*[1]; M. Witthaunt[1]; D. Neuschutz[1]; [1]Rheinishch-Westfalische Technische Hochschule Aachen, Lehrstuhl fur Theoretische, Aachen D-52056 Germany

Metastable ceramic coatings are gaining increased attention in industrial applications. One of the most familiar is the wear resistant (Ti,Al)N coatings which is extensively used for the protection of cutting tools. Another example of ternary metastable films with superior performance in comparison to the stable constituent binaries is Al-O-N. The high chemical and thermal stability of Al-O-N makes this film an attractive candidate for diffusion barriers in gas turbines. Due to the non-equilibrium conditions of physical vapor deposition, this technique is exceptionally suitable for the deposition of metastable films. The presented paper will focus on the particularities of physical vapor deposition and characterization of metastable ternary coatings. As many metastable solution phases do not form crystalline phases, special attention will be paid to the analysis of the binding states of the components by Auger-and Photoelectron spectroscopy. It will be shown that the analysis of binding states and electronic structure is a powerful tool for the determination of the properties of metastable solution phases and their enhancement for technical application.

12:05 PM
DEVELOPMENT OF HARDFACING CONSUMABLE MATERIAL FROM IRON CARBIDE: *Brajendra Mishra*[1]; David L. Olson[1]; David Fazzina[1]; [1]Colorado School of Mines, Dept. of Metallurgical and Materials Engineering, Center for Welding, Joining, and Coatings Research, Golden, CO 80401 USA

A novel hardfacing consumable material has been development using commercial grade iron carbide and ferro-titanium. The process of forming titanium carbide particles in a martensic matrix from these reactants, passing through the welding arc into the weld deposit, is inexpensive. The product phases provided high hardness and superior wear properties. With optimal composition and processing conditions, weld deposits have been produced which show notable levels of wear resistance. The flux coated arc welding with shielding gas was used for this purpose. Penetration in weld-deposits was achieved by enhancing the exothermically assisted reactions leading to the proper formation of weld beads for hardfacing. The weld bead size and morphology was improved by switching from an argon-carbon dioxide gas to a nitrogen shielding gas. The optimum microstructure consisted of carbides which are imbedded in a martensite matrix with some retained austenite. Key considerations in further optimization of the weld microstructure included reducing the free silicon by the addition of molybdenum and the addition of aluminum to reduce the amount of oxygen. It has been demonstrated that excess oxygen acts to reduce the amount of carbon and titanium available to react and form titanium carbide.

12:20 PM
STRESSES GENERATED ON ALUMINUM AS THE FUNCTION OF APPLIES POTENTIAL AND pH IN PRESENCE OF CHLORIDE: *S. E. Benjamin*[1]; F. A. Khalid[2]; [1]Colorado School of Mines, Dept. of Metallurgy and Materials Engineering, Golden, CO 80401 USA; [2]Gulam Ishaq Khan Institute of Engineering Science & Technology, Faculty of Metallurgy and Materials Engineering, Topi Pakistan

The resistance of the oxide film on aluminum is imperiled by the stresses generated during growth of the oxide. The present studies focus upon the stresses generated on aluminum as the function of the applied potential in sulfuric acid solutions of different strengths containing chloride ions. The resulting current depicts the formation/dissolution of the oxide which is controlled both by the pH and the chloride anion. The magnitude and direction of stresses generated during the anodic oxidation process are measured by the beam deflection technique. The results have been interpreted in terms of the formation and annihilation of the anion (O2-) and the cation (Al3+) vacancies. Reduction in the aluminum ion vacancies (VAl3+) results in the compressive stress deflection whereas, tensile stress deflection is introduced due to an increase in the oxygen ion vacancies (VO2-).

SYNTHESIS OF LIGHTWEIGHT METALS III: Titanium - III

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. Centre, Farnborough, Hampshire GUI14OLX UK; D. Eliezer, Ben Gurion University, Dept. of Mats. Eng., Neqev Israel; P. G. McCormick, University of W. Australia, Res. Centre for Adv. Min. & Mat. Proc., Nedlands, W.A. 6907 Australia

Wednesday AM Room: 10
March 3, 1999 Location: Convention Center

Session Chairs: J. Ma, Beijing Institute of Aeronautical Materials (BIAM), Beijing 100095 China; P. G. Partridge, DERA, Struct. Mats. Centre, Farnbourough, Hans GU14 6TD UK

8:30 AM INVITED PAPER
OVERVIEW OF TITANIUM GOLF CLUBS - PART I: *Jimin Ma*[1]; Chenggong Li[1]; F.H. (Sam) Froes[3]; [1]Beijing Institute of Aeroautical Materials (BIAM), P.O. Box 81, Beijing 100095 China; [3]University of Idaho, IMAP, Mines Bldg., Rm. 321, Moscow, ID 83844-3026 USA

Titanium is ideally suited for many golf club applications including woods and putters. The case for titanium irons is less clear. This paper will discusss the development of new titanium concepts for irons including tungsten weighting to lower the center of gravity of the head.

8:50 AM INVITED PAPER
OVERVIEW OF TITANIUM GOLF CLUBS - PART II: *Jimin Ma*[1]; Chenggong Li[1]; F.H. (Sam) Froes[3]; [1]Beijing Institute of Aeroautical Materials (BIAM), P.O. Box 81, Beijing 100095 China; [3]University of Idaho, IMAP, Mines Bldg., Rm. 321, Moscow, ID 83844-3026 USA

Titanium is ideally suited for many golf club applications including woods and putters. The case for titanium irons is less clear. This paper will discusss the development of new titanium concepts for irons including tungsten weighting to lower the center of gravity of the head.

9:30 AM

CONSOLIDATION, MICROSTRUCTURE AND PROPERTIES OF TAPE-CAST Ti / SiC FIBRE COMPOSITES: *Z. X. Guo*[1]; C.M. Lobley[1]; Q. Kang[1]; [1]University of London, Dept. of Mats., Queen Mary and Westfield College, Mile End Rd., London E1 4NS UK

Light weight composite based continuous SiC fibres and titanium matrices offer very desirable combinations of high-temperature strength, stiffness, and creep resistance, which are ideal for various components in the future generation of gas and steam turbine engines. However, large-volume applications are currently hampered by the relatively high cost of the material. A great percentage of the cost is due to its manufacturing. A low-cost tape-casting processing technique has been under study at our laboratory. The process uses relatively large inexpensive matrix alloy powders mixed with an organic binder to form a slurry, which is then cast to form a thin uniform powder tape. Once dried, the tape is laid-up with filament-wound SiC fibres and consolidated in a vacuum hot press, with a burnout dwell at moderate temperatures to ensure removal of the organic components. This paper concentrates on the study of the consolidation process of tape-cast powder/fibre preforms. The effects of temperature, pressure and time on consolidation kinetics were evaluated. Microstructural examination of both partially and fully consolidated composites was carried out by means of optical, SEM and TEM analyses to identify matrix flow behavior, microstructural evolution, and integrity of the composites. Composites of very uniform fibre distribution with no fibre damage have been achieved. The as-processed composites were extensively tested under tension and four-point bending. The results show that the average strength of the composites reaches at least 92% of the law-of-mixtures value. This is comparable to values obtained on similar composites manufactured by alternative processes. However, a considerable cost saving and a high degree of product flexibility are realised from the tape-casting route.

9:50 AM

SYNTHESIS AND CHARACTERIZATION OF TITANIUM-BASED INTERMETALLIC / METALLIC LAMINATES: *C. B. Loader*[1]; S. J. Howard[1]; C. Malcolm Ward-Close[1]; [1]DERA Farnborough, Structural Mats. Centre, Room 2008, A7 Bldg., Farnborough, Hampshire GU14 OLX UK

Titanium aluminides are a potential replacement for the current aerospace alloys, at present however their low room temperature toughness and ductility limits their application. Introducing a ductile phase into the intermetallic matrix has been shown to increase the effective toughness of the composite material. Three methods were selected for the fabrication of titanium/titanium aluminide laminates; diffusion bonding, electron beam physical vapour deposition and vacuum plasma spraying. The resultant laminated composite materials were expected to process both high temperature creep resistance and low temperature ductility. Microstructural evaluation of the laminates was performed and mechanical property data was generated. Results show the strength and toughness variation obtained in multi-layered materials compared to monolithic materials.

10:10 AM BREAK

10:25 AM

IMPACT TOUGHNESS OF LAMINATES COMPOSED OF LAYERS OF TITANIUM-ALLOY AND TITANIUM-ALLOY MMC: *Y. Q. Zuo*[1]; D. Smith[1]; P. G. Partridge[2]; A. Wisbey[2]; [1]University of Bristol, Dept. of Mech. Eng., Queens Bldg., University Walk, Bristol, Avon BS8 1TR UK; [2]DERA, Farnborough, Structural Materials Centre, Farnbourough, Hants GU14 6TD UK

Instrumented impact toughness values in bend have been obtained for symmetrical 3-layer laminates composed of diffusion bonded IMI 834 Ti-alloy and Ti-6Al-4V alloy/continuous SiCr metal matrix composite (MMC) sheets. The MMC represented 50 volume % of the laminate and was present as either a single layer at the midplane (C-type laminate) or as two thinner layers at the surfaces of the laminate (S-type laminate). Control test pieces consisted of 100% IMI 834 and 100% MMC and notched and unnotched test pieces were used. The laminate microstructure was particularly effective in increasing the notched impact strength relative to both the IMI834 Ti-alloy and the MMC. The impact toughness could be predicted in terms of the work to initiate fracture and to propagate a crack in this system. The modulus value for the S-type laminate with only 50% MMC (192 GPa) was within about 4% of the value for the 100% MMC test piece. The laminate allows cost effective utilisation of the MMC and a lower density compared with monolithic Ti-alloy. It will be shown that the laminate has a unique overall combination of properties.

10:45 AM

HIGH-TEMPERATURE TRIBOLOGICAL BEHAVIOR OF Ti-V ALLOYS AND Ti-40Mo: *Xu Huang*[1]; Jimin Ma[1]; Chunxiao Cao[1]; Bao Wang[1]; Yang Gao[1]; Yaohe Zhou[2]; [1]Beijing Institute of Aeronautical Materials (BIAM), P.O. Box 81-15, Beijing 100095 China; [2]Northwestern Polytechnical University, Xi'an 710072 China

Generally combustion property of titanium alloy is related closely to its friction behavior. The variations of unlubricated sliding friction coefficients and wear rates vs temperature up to 900℃ for Ti-20V, Ti-40V and Ti-40Mo alloys were determined by pin-on-disc tribometer. The results show that the friction coefficients and wear rates decrease with increasing temperature, and decrease sharply at 700℃ for the Ti-V alloys and 800℃ for Ti-40Mo alloy, that the friction coefficient of Ti-40V is lower than that of Ti-20V. The morphology of friction surfaces and composition of oxide scales formed on the surfaces were examined by SEM-EDAX. The structures of transferred oxides from Ti-20V, Ti-40V were analyzed by XRD. It is suggested that the decrease of friction coefficients and wear rates of the Ti-V alloys and Ti-Mo alloy at elevated temperature is resulted from the lubrication due to the formation of soft, liquid V_2O_5 or MoO_3 oxide.

11:05 AM

THE PRODUCTION OF MAGNESIUM-TITANIUM ALLOYS BY MECHANICAL ALLOYING: *Simon B. Dodd*[1]; Susan Morris[1]; [1]DERA, Structural Materials Centre, Griffith Building (A7), DERA Farnborough, Hampshire GU14 0LX UK

In this paper the development of a mechanical alloying (MA) production technique for novel magnesium titanium binaries will be discussed. The aim of the work was to develop complete solid solution of titanium in a magnesium matrix for use as structural corrosion resistant lightweight alloys. The alloy range under investigation ranged from 0 to 20 wt% Ti. Previous work using physical vapour deposition (PVD) had demonstrated the potential of the alloy system for corrosion resistance and indicated that alloys under 20 wt% Ti provide a good balance between corrosion resistance and density. Traditionally the use of magnesium alloys, especially in aerospace applications, has been limited by the perceived poor corrosion resistance. The addition of titanium produces both a self-healing corrosion layer and reduced galvanic potential. The boiling point of magnesium is lower than the melting point of titanium and only novel processing routes such as MA and PVD can be successfully utilised to produce alloys of magnesium and titanium. This paper will describe the work carried out to develop an MA process route for solid solution Mg-Ti alloys. The influence of various process control agents on the synthesis of Mg-Ti solid solutions will be discussed. In addition, this paper will detail some of the material properties obtained from these novel materials.

11:25 AM

SYNTHESIS OF TITANIUM-VANADIUM MASTER ALLOYS BY MECHANOCHEMICAL PROCESSING: *E. G. Baburaj*[1]; Tri Widodo[1]; F .H. (Sam) Froes[1]; [1]University of Idaho, IMAP, Mines Bldg., Rm. 321, Moscow, ID 83844-3026 USA

Titanium-vanadium master alloys are extensively used for the preparation of Ti-Al-V alloys. The present work is an attempt to produce the high melting Ti-V alloys in powder form by co-reduction of chlorides of Ti and V. Stoichiometric amounts of $TiCl_4$ and VCl_3 corresponding to the alloy composition $Ti_{50}V_{50}$ have been milled together with the reducing agents CaH_2 and Mg in a spex mill. The reaction product after leaching consisted of hydrides of Ti and V. It is not clear whether the hydrides have mutual solubility of one element in the hydride of the other. Further work on dehydrogenation and consolidation is in progress.

THE MARTIN E. GLICKSMAN SYMPOSIUM ON SOLIDIFICATION AND CRYSTAL GROWTH: Microgravity Processes

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

Wednesday AM Room: 11A
March 3, 1999 Location: Convention Center

Session Chairs: Robert S. Sokolowski, IGC, 1875 Thomaston Ave., Waterberry, CT 06704 USA; Ed Winsa, NASA Lewis Research Center, Space Div., Cleveland, OH 44135 USA; Matthew Koss, R.P.I., Dept. of Mats. Sci. & Eng, Troy, NY 12180 USA

8:30 AM INTRODUCTION

8:45 AM
SOLIDIFICATION BEHAVIOR OF BINARY ORGANIC EUTECTICS AND MONOTECTICS; 1,2,4,5-TETRACHLOROBENZENE-M-AMINOPHENOL SYSTEM: *Uma Shanker Rai*[1]; [1]Banaras Hindu University, Chemistry Dept., Varanasi, UP India

With a view to study the solidification behaviour of binary organic eutectics and monotectics, phase-diagram, growth behaviour and microstructure of 1,2,4,5-tetrachlorobenzene and m-aminophenol system were studied.

9:15 AM
EVOLUTION OF SIDEBRANCH SPACINGS IN THREE-DIMENSIONAL DENDRITIC GROWTH: *Christoph Beckermann*[1]; Qiao Li[1]; [1]University of Iowa, Mechanical Engineering, 2412 EB, Iowa City, IA 52242 USA

The sidebranching behavior in three-dimensional dendritic growth is investigated through a detailed measurement of the arm spacings of succinonitrile (SCN) dendrites using images from the microgravity experiments of Glicksman and coworkers. The measurements show that the sidebranching evolution is divided into two regimes: an initial linear regime and a subsequent non-linear coarsening regime. A simple model, based on the Mullins-Sekerka linear stability theory, is developed to describe the initial sidebranching behavior and is found to be in excellent agreement with the experimental results. In the non-linear regime, the measured arm spacings are compared with previous coarsening theories. It is found that a careful distinction between arm spacings and curvatures is necessary to explain the measurements.

9:35 AM
EFFECT OF STABILIZING TEMPERATURE GRADIENTS ON THERMAL CONVECTION IN PHYSICAL VAPOR TRANSPORT OF HG2CL2: *J. W. Choi*[1]; M. H. Kwon[2]; S. K. Kwon[3]; G. T. Kim[1]; Martin E. Glicksman[4]; [1]Hannam University, Chemical Engineering Dept., 133 Ojung-Dong, Taejon 306-791 Korea; [2]SKC Company, R&D Center, Songgu, Chonan 330830 Korea; [3]Agency of Defense Development, Taejon 305600 Korea; [4]R. P. I., Materials Sci.& Eng. Dept., Troy, NY 12180-3590 USA

Mercurous chloride (Hg2Cl2) crystals hold promise for many acousto-optic and opto-electronic applications. This material is prepared in closed ampoules by the physical vapor transport (PVT) growth methods. Due to the temperature gradient between the source and the growing crystal region which is the driving force for mechanism of PVT, i.e., evaporation-condensation, the thermal buoyancy-driven convection may occur. The thermal boundary conditions established by imposing different temperature on sidewalls of the enclosure cause simultaneous horizontal and vertical convective flow in the PVT of Hg2Cl2. It is found that for the ratios of horizontal to vertical thermal Rayleigh numbers RaH /Ra = 1.5, the convective flow structure changes from multicellular to unicellular for the base parametric state of Ra = 2.79 x 104, Pr = 0.91, Le = 1.01, Pe = 4.60, Ar = 0.2 and Cv = 1.01. The vertical gradient tends to destabilize the flow that leads to oscillations. This paper will present the effect of stabilizing temperature gradients on thermal convection for various aspect ratios (widt h-to-transport length).

9:55 AM INVITED PAPER
A COMPARISON OF MORPHOLOGICAL INSTABILITY AND OTHER INTERFACIAL INSTABILITIES: *Ranga Narayanan*[1]; [1]University of Florida, Dept. of Chemical Engineering, Gainesville, FL 32611 USA

This is a review talk and will focus on the solidification instability of interface morphology. I shall compare this classical problem with another classical problem in fluid mechanics i.e., the Marangoni instability problem. There will be a discussion of interface morphology changes when convection occurs for solidification of pure substances and for solidification of a dilute binary alloy. I shall also relate some of the phenomena with the instabilites that occur during an electro-deposition process.

10:15 AM BREAK

10:35 AM INVITED PAPER
WHY WE WERE WRONG ABOUT THE EFFECT OF CONVECTION ON DENDRITIC GROWTH IN MICROGRAVITY: *Mathew Koss*[1]; [1]R. P. I., Materials Science and Engineering Dept., Troy, NY 12180 USA

The Isothermal Dendritic Growth Experiment (IDGE), a NASA sponsored series of Space Shuttle microgravity experiments, was designed and operated to grow and photograph dendrites, the ramified tree like morphology assumed by many liquid-solid solidification interfaces, in the absence of convective heat transfer. This data from this experiment forms a benchmark for fundamental tests of dendritic solidification theories. The first space flight of the IDGE in March of 1994 provided a rich data set from which we published many new results and conclusions. But, subsequent analysis, additional theoretical work, and the data from the second IDGE space flight experiment in March of 1996 showed that one of our first published conclusions was wrong. How and why we made, eventually recognized, and corrected this error is an interesting and important story for the scientific community in general, and NASA's microgravity science community in particular.

11:05 AM
THE INFLUENCE OF INTERFACE MORPHOLOGY ON HEAT TRANSPORT IN DENDRITIC SOLIDIFICATION: *Jeffrey C. LaCombe*[1]; *Matthew B. Koss*[1]; Douglas C. Corrigan[1]; Afina Lupulescu[1]; Laura Tennenhouse[1]; Martin E. Glicksman[1]; [1]Rensselaer Polytechnic Institute, Materials Science and Engineering, CII Building, Room 4219, Troy, NY 12180 USA

The method of moving heat sources is applied to the problem of dendritic growth in a quiescent, isothermal melt. By specifying various solid-liquid interface shapes in the model formulation, a clear understanding of the influence of the tip shape and the side-arm cruciform is obtained. The results of this study provide an explanation of several aspects of the microgravity-conducted Isothermal Dendritic Growth Experiment (IDGE). When corrections to Ivantsov's paraboloidal tip shape are incorporated into the transport solution to reflect the actual observed tip shape, enhanced agreement with the experimental data results. Additionally, these conclusions support earlier work by Schaefer (J. Cryst. Growth, vol. 43, p. 17) in suggesting that under the conditions of the IDGE experiment, the side-branch region of a dendrite can contribute significantly to the thermal field at the tip. Furthermore, the growth process is not sensitive to the details of the tip shape, provided the interface is largely paraboloidal. These suggest that the scatter in the IDGE data can be explained by stochastic variations in the side branch

structure, and the corresponding influence that this region has upon the transport processes at the tip. With these results, it is now reasonable to claim that the basic transport solution describing dendritic growth is correct, provided details such as container wall effects and dendrite self-interaction are accounted for. Until now, these conclusions have not been completely supported by quantitative evidence. Furthermore, these results suggest that the side branch region of a dendrite affects the transport portion of the dendritic growth problem as well as the scaling portion.

11:25 AM

UNDERCOOLING EFFECTS ON DROPLETS COARSENING IN THE Cu-Co SYSTEM: *Delin Li*[1]; Michael B Robinson[2]; Thomas J Rathz[3]; [1]NASA/MSFC NRC, Space Sciences Lab, Drop Facilities, ES75, Huntsville, AL 35812 USA; [2]NASA/MSFC, Space Sciences Lab, ES71, Huntsville , AL 35812 USA; [3]UAH, Materials Processing Lab, Huntsville, AL 35899 USA

The Cu-Co system is often chosen to study Ostwald ripening through aging treatment or liquid phase sintering, because of its low misfit strain and a similar mass density between Co and Cu. It has been shown that the growth of decomposed or sintered particles basically obeys the well-known LSW theory, though there are discrepancies about the coarsening rate and size distribution. Another attraction of the binary Cu-Co system is the potential thermodynamic tendency to immiscibility upon undercooling. This allows a study of phase separation process and droplet coarsening in a metallic liquid-liquid mixture where the amount of experimental data obtained to date is scarce. In this paper, liquid phase separation and droplet growth were investigated for a near-critical Cu50Co50 and an off-critical Cu68Co32 composition (atomic) by means of undercooling experiments. It was observed that liquid phase separation could occur at about 50 K below the miscibility gap, while the two resultant melts were further undercooled by larger than 300 K prior to solidification. The droplet growth behavior was found to exhibit three regimes: a power law growth, linear growth, and saturation stage. From microstructural examinations, it turned out that in addition to dendrites and droplet-like morphology reported previously, an interconnected structure was observed for the near-critical composition at intermediate undercooling. This interconnected structure played a crucial role in droplet coarsening at high undercooling.

11:45 AM

SINGLE ROLL CASTING OF ALUMINIUM ALLOY STRIP: *Daniel Liang*[1]; Wendy E. Borbidge[1]; Ross V. Allen[1]; [1]CSIRO, Materials Science and Technology, Private Bag 33, Clayton South MDC, Victoria 3169 Australia

Al-Si alloy strip has been produced by use of a single roll casting assembly with or without an additional deforming roll. The assembly has been configured to overcome defects such as porosity and surface ripples. The mechanisms for the defect formation were investigated as a function of operational parameters, strip thickness and deforming load. Internal microstructures were characterised for various solidification conditions. Results show that strips of 1 to 6mm thick with sound internal microstructures and satisfactory surface quality can be obtained by using the modified single roll casting assembly.

Institute of Metals Lecture and Robert F. Mehl Medalist
Time: 12:00 Noon
Room: 6E
Location: San Diego Convention Center

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

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

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

Program Organizers: Robert Schiffman, R.S. Research Inc., Barton, VT 05822 USA; Carlo Patuelli, Universita di Bologna, Departimento di Fisica, Bologna I-40126 Italy

Wednesday PM Room: 15B
March 3, 1999 Location: Convention Center

Session Chair: Mike Robinson, MSFC, MSFC, AL 35812

2:00 PM

INTRODUCTION TO CONTAINERLESS PROCESSING: *Michael Wargo*[1]; Shinichi Yoda[2]; Rainer Kuhl[3]; Philip Gregory[4]; [1]NASA Headquarters, Code UG, Washington, DC 20546 USA; [2]NASDA, Space Utilization Research Center, Sengen, 2-1-1, Tsukuba-shi, Ibaraki-ken 305 Japan; [3]DLR, Koenigswinterer Str. 522-524, Bonn, 53227 Germany; [4]Canadian Space Agency, 6767 Route de L'Aeroport, St-Hubert, Quebec J3Y 8Y9 Canada

Containerless processing is the most promising technology for enabling new types of material production through deep supercooling, taking highly precise thermophysical properties measurements, and making highly purified materials. The development of hardware related to this technology for International Space Station utilization has been supported independently by NASDA, DLR, and CSA, each providing facilities with different positioning technologies. Each positioning method has an advantage for some particular microgravity experiments. ISS is expected to be used collaboratively by all participating countries for the study of the microgravity sciences, and it is hoped that these containerless facilities will be able to completely cover all of the microgravity sciences requiring containerless processing with each method contributing best to a particular science study. The purpose of this workshop is as follows. Firstly, we will try to define the science envelope which could be covered by the containerless proce ssing methods in microgravity. Secondly, if there is a science area which is not covered by one of the existing containerless processing methods, we will try to determine a possible scenario by which it could be covered, which may involve modification of one of the existing containerless processing methods. Thirdly, we will provide recommendations to the participating agencies for any perceived short-comings or modifications of the containerless processing facilities in order for these facilities to cover the necessary studies contained within the defined science envelope. In general, the experimental facilities for ISS should be well matched for performing a particular science study in order to get fruitful experimental results necessary for the benefit of humankind.

2:20 PM

TEMPUS CONTAINERLESS PROCESSING FACILITY FOR SPACE STATION - PRELIMINARY DESIGN AND SPECIFICATION: *Joerg Piller*[1]; [1]Dornier GmbH, Daimler-Benz Aerospace, Friedrichshafen D-88039 Germany

The containerless processing facility TEMPUS was successfully used for electromagnetic levitation experiments during the MSL-1 Spacelab mission in 1997. Scientific goals have been the study of nucleation statistics and solidification speeds in undercooled melts, and the determination of thermophysical properties of the melt above and below the melting point. For future research in this promising field the accommodation of an Advanced TEMPUS facility on board of the International Space Station is under discussion. The results of a design study are presented to show that the well-proven technology of TEMPUS Spacelab can be transferred to a Space Station facility. A set of samples will be processed in experiment containers which will be exchanged together with coil system, windows, stimuli or other specific devices.

2:40 PM

ELECTROMAGNETIC LEVITATION IN MICROGRAVITY: EXPERIMENTS AND RESULTS OF THE TEMPUS TEAM: *Ivan Egry*[1]; [1]DLR, WB-RS, Institut fuer Raumsimulation, Cologne 551140 Germany

Electromagnetic levitation is a convenient tool for containerless processing of electrically conducting materials. In microgravity, only small stabilizing forces are needed; therefore, positioning and heating can be decoupled. The TEMPUS facility is a realization of an electromagnetic levitation facility designed to operate in microgravity. It allows to study properties and nucleation behavior of undercooled metallic melts. During recent Spacelab flights, experiments have been performed on a number of different materials. Thermophysical properties, such as specific heat, viscosity, surface tension, thermal expansion were measured, and the nucleation behavior as well as the growth velocity of the nucleated stable or metastable phases were studied. In this paper, an overview of the experimental approaches and the results obtained will be given.

3:00 PM

ELECTROSTATIC LEVITATION FURNACE (ELF) FOR THE JAPANESE EXPERIMENT MODULE (JEM): *Hiroki Karasawa*[1]; [1]NASDA, Space Utilization Research Center, Sengen, 2-1-1, Tsukuba-shi, Ibaraki-ken 305 Japan

The Electrostatic Levitation Furnace (ELF) for the Japanese Experiment Module (JEM) can treat many kinds of materials such as metals, semiconductors, and ceramics. The position of the experiment sample is controlled by the electrostatic force between the charged sample and eight independently controlled electrodes whose voltage are determined by the feedback control system using the sample positioning signals detected by 2-axis CCD cameras. The samples will be heated by four lasers. The lasers' power can be controlled independently, and it is possible to perform experiments under vacuum condition or some kind of gas atmosphere. ELF provides various observation capabilities such as a pyrometer, a thermal imaging system, and a video camera. The Preliminary Design Review (PDR) of ELF will be held in March 1999. Preliminary specifications and breadboard model test results will be presented.

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EXPERIMENTS PERFORMED BY THE ELECTROSTATIC LEVITATION FURNACE (ELF): *Naokiyo Koshikawa*[1]; [1]NASDA, Space Utilization Research Center, Sengen, 2-1-1, Ibaraki-ken, Tsukuba-shi 305 Japan

Electrostatic levitation is a useful processing method which enables us to process any kind of materials including insulators such as ceramics. As an example, we will show you the preliminary result of the undercooling experiment of BiFeO3 in microgravity performed by using the Electrostatic Containerless Furnace by sounding rocket TR-IA#7. The capability of the Electrostatic Levitation Furnace for ISS is widespread, but the most characteristic point is "lowest turbulence" which gives us accurate physical properties measurements and larger undercooling.

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CONTAINERLESS RAPID SOLIDIFICATION FROM UNDERCOOLED MELT OF OXIDE MATERIALS : *Kazuhiko Kuribayashi*[1]; [1]The Institute of Space and Astronautical Science, 3-1-1 Yoshinodai, Sagamihara, Kanagawa Japan

Abstract not availale.

4:20 PM
OVERVIEW OF SPACE-DRUMS - A DYNAMICALLY CONTROLLED MULTI-BEAM ACOUSTIC LEVITATOR-POSITIONER: *Philip Gregory*[1]; [1]Canadian Space Agency, 6767 Route de l'Aéroport, St-Hubert, Québec J3Y 8Y9 Canada

Space-DRUMS is a new approach for positioning, manipulating, and shaping samples in both gravity and microgravity environments. It relies on the direct acoustic radiation force from many equivalently-positioned ultrasonic beams under dynamic feedback control to leviate or position large samples.

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SCIENCE TO BE PERFORMED ON SPACE-DRUMS: *Rodney Herring*[1]; [1]Canadian Space Agency, 6767 Route de l'Aéroport, Québec , St-Hubert 8Y9, J3Y Canada

Space-DRUMS is designed to support a full range of containerless material processes in a microgravity environment. Acoustic radiation forces will be used to position specimens during scientific investigations.

ALUMINA AND BAUXITE: Silica Chemistry in the Bayer Process

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

Wednesday PM Room: 6E
March 3, 1999 Location: Convention Center

Session Chair: Dr. Peter McIntosh, Kaiser Aluminum & Chemical Corporation, Pleasanton, CA USA

2:00 PM
THE KINETICS OF SEEDED CRYSTALLIZATION DESILICATION OF SYNTHETIC BAYER LIQUOR: *Jonas Addai-Mensah*[1]; Mark C. Barnes[1]; Andrea R. Gerson[1]; [1]University of South Australia, Ian Wark Research Institute, The Levels, Adelaide 5095 Australia

Crystal growth kinetics of pure sodalite, pure cancrinite and their phase mixtures resulting from seeded-desilication of synthetic Bayer liquor have been studied under isothermal, batch precipitation conditions. The temperatures and concentrations used were similar to those at which sodium aluminosilicate scale forms in alumina plant heart exchangers. Sodalite and cancrinite seeding resulted in faster desilication rate and the suppression of scale formation. An activation energy of 30 kj per mol and a second order dependence of the desilication rate on SiO2 relative supersaturation were estimated for sodalite crystal growth. For cancrinite, the rate depended on SiO2 relative supersaturation to the power of 3 with an activation energy of 80 kj per mol. A model for sodalite-cancrinite mixed-phase precipitation showed that the observed kinetics are simply a linear combination of those exhibited by pure crystal growth. It appears that theoretical modelling of sodalite and cancrinite may be achieved using 2 Dimensional Nucleation theories.

2:30 PM
REDUCING ALUMINA PRODUCTION COSTS: *Ronald F. Nunn*[1]; [1]The Winters Company; Tucson, Arizona USA

Alumina is an essential raw material for the production of aluminum in electrolytic cells. There are about 50 operating alumina plants worldwide producing more than 40 million tpy of metal grade alumina by the Bayer process. The cash cost of producing alumina in these plants varies from less than $100/tonne to more than$200/tonne for a number of different reasons. This large variation suggests considerable potential cost savings. Alumina is a worldwide commodity, as a result, very few alumina plants can consider themselves insulated from international competition. Over the next 10 years, about 9 million tonnes of additional alumina capacity is forecast to come on stream. A useful tool for worldwide alumina plant operating cost curve. The bulk of new capacity will no doubt be installed in the plants with low production costs at the bottom end of the cost curve. As a result, those plants at the high end of the curve today will be pushed even higher on the cost curve and potentially out of existence. This paper examines the factors influencing the cost of the major items involved in the cost of producing alumina, including bauxite, caustic soda, fuel, power, labot and maintenance. It then reviews methods for reducing production costs, including improved technology, which will improve a plant's position on the cost curve and make it more competitive.

3:00 PM
SODALITE-CANCRINITE PHASE TRANSFORMATION, KINETICS, AND SOLUBILITY IN BAYER LIQUOR: *Jonas Addai-Mensah*[1]; Mark C. Barnes[1]; Andrea R. Gerson[1]; [1]University of South Australia, Ian Wark Research Institute, The Levels, Adelaide 5095 Australia

The equilibrium solubility of pure sodalite and pure cancrinite crystals in systhetic, spent Bayer liquor has been determined over a range of temperatures and as a function of liquor concentration of NaOH and Al(OH)3. The solubility of both sodalite and cancrinite increased linearly with increasing temperature. For cancrinite, increasing the concentration of NaOH and Al(OH)3 increased solubility dramatically. The mechanism and kinetics of sodalite transformation to cancrinite was investigated under a variety of conditions. The transformation was observed to involve a solution-mediated mechanism with sodalite disolution and subsequent nucleation and growth of cancrinite crystals. Furthermore, the transformation of reaction rate was found to be first order with respect to the relative concentration of sodalite. Over the temperature range of 160-240ϒC, an activation energy of 133 kj per mol was estimated for the overall mechanism .

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CHARACTERIZATION OF SYNTHETIC ALUMINA TRIHYDRATE CRYSTALS AND BAYER LIQUORS BY THERMAL ANALYSIS: *Jonas Addai-Mensah*[1]; [1]University of South Australia, Ian Wark Research Institute, The Levels, Adelaide 5095 Australia

Modulated and Standard Differential Scanning Calorimetry and Thermogravimetric analysis of several crystalline Al(OH)3, amorphous Al(OH)3 and Bayer liquors have been carried out. The analysis of reversing and non-reversing heat flows showed that the enthalpic events taking place during thermal decomposition are dependent upon particle formation history and structure. The changes in solids specific heat capacity were observed to be influenced by particle size, crystallinity and agglomerate porosity. For synthetic, supersaturated sodium and potassium aluminate liquors, the specific heat capacity decreased dramatically with decreasing concentration of uncoordinated, bulk water. Furthermore, caustic and caustic aluminate solutions made from NaOH appear to have a higher concentration of bulk water than equivalent solutions made from KOH. The difference between bulk water content of potassium and sodium liquors is believed to be associated with the extent of ion-pairing and water coordination abilities of solution Na+ and K+ ions.

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THE SYNTHESIS OF THE PURE Al2O3 LAYERS ON THE SINTERED CORUNDUM CUTTING TOOLS BY THE CVD METHOD: Andrzej Kwatera[1]; Wojciech Tomaszewski[1]; *Mariusz A. Wójcik*[1]; Julian Plewa[2]; Horst Altenburg[2]; [1]Academy of Mining and Metallurgy, Faculty of Ceramic and Materials Engineering, Av. Mickiewicza 30, A-3, Cracow 30-059 Poland; [2]Fachhochschule Munster, Fachbereich Chemieingenieurwesen, Stegerwaldstrasse 39, Steinfurt, Munster D-48565 Germany

The initial conditions of the synthesis of the pure and high density Al2O3 layers on the sintered corundum cutting tools by the CVD method was presented in this paper. The alumina metalorganic compounds were used in the investigations. Results shown that high density and well adhered Al2O3 layers were obtained on cutting tools substrates with the deposition rate of 3,5um/min. Obtained layers can be applicated

for the manufacture of the precise robot parts with exactly controlled chemical composition giving the cutting speed about 900m/min.

ALUMINUM ALLOYS FOR PACKAGING IV: Session II — Fundamental Studies

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

Wednesday PM Room: 3
March 3, 1999 Location: Convention Center

Session Chairs: Subodh K. Das, ARCO Aluminum, Inc., Louisville, KY USA; John E. Adams, Metal Container Corporation, St. Louis, MO 63127-1218 USA

2:00 PM
TEXTURE EVOLUTION AND CORRESPONDING FORMABILITY OF AA 3104 ALUMINUM ALLOYS DURING COLD ROLLING: *Xiang-Ming Cheng*[1]; Yansheng Liu[1]; James G. Morris[1]; [1]University of Kentucky, Light Metals Research Laboratories, Dept. of Chemical And Metallurgical Engineering, College of Engineering, 177 Anderson Hall, Lexington, KY 40506 USA

The deformation behavior of can body aluminum alloys is mainly determined by crystallographic texture. The original hot band texture and the cold rolling process have significant influences on the ultimate texture and thus on the formability. AA 3104 aluminum alloy has been used in this investigation. Before cold rolling the materials have been annealed at certain conditions in order to obtain a fully recrystallized microstructure. Samples at different cold rolling reductions have been prepared for cup testing and crystallographic texture determination. By comparing texture components and the corresponding earing results, a better understanding of the relation between crystallographic texture components and earing is expected. Several degrees of reduction have been employed, especially reductions near the critical point which leads to a change of earing from 90 degrees to 45 degrees. In addition, different heating rates of the hot band have been used to obtain different original textures for the important effect on texture evolution and the resulting ultimate earing behavior.

2:20 PM
CONSTITUTIONAL RELATIONSHIPS FOR THE HOT WORKING OF AA 3004 (Al-1.0 Mn-1.2Mg): *J. Belling*[1]; Hugh McQueen[1]; [1]Concordia University, Mechanical Engineering, Montreal H3G 1M8 Canada

Recrystallized plate of 3004 (0.96% Mn, 1.23%Mg, 0.37Fe) was subjected to hot torsion tests in the ranges 250° to 500°C and 0.1 to 10 s-1. The flow curves strain hardened to a broad peak and softened slightly towards a steady state regime. At higher temperature, T and lower strain rate E the maximum stress s and the softening were lower and the fracture strains were higher. The exponential law was found satisfactory, but the power law was not. The constants A, n, Q HW for the equation: A(sinh as)n = E exp (QHW/8.31 T) were derived for a ranging from 0.01 to .008 MPa -1. The constants differed slightly for longitudinal and transverse specimens. The use of a = 0.04 or 0.06 MPa -1 makes comparison with published data simpler; the agreements were reasonable given the variations in composition. Optical microscopic examination revealed elongated grains in which the subgrains became more clearly defined as T rose and E diminished. Clearly dynamic recovery provided good hot workability through a substructure with reduced strain energy which also inhibited recrystallization unless the product is heated to about 50° above the deformation temperature as previously published.

2:40 PM
INVESTIGATION OF LOW RESOLUTION TEXTURE ANALYSIS FOR ON LINE R- VALUE DETERMINATION OF CAN BODY MATERIALS: *Y. Liu*[1]; X. M. Cheng,[1]; Y.L. Liu[1]; C.S. Man[1]; J. G. Morris[1]; [1]University of Kentucky, Light Metals Research Laboratories, Dept. of Materials and Chemical Engineering, Lexington, KY 40506 USA

Aluminum alloys for can body making are produced by hot and cold rolling. The hot band or annealed hot band is the initial condition for subsequent cold rolling. Excellent deep drawability is mainly determined by the initial texture of the hot band if the cold reduction is constant. On line determination of the Lankford parameter (R-value) for the hot band is very important to industrial practice. In the present paper, hot bands of direct chill cast (DC) and strip cast (SC) AA3004 aluminum alloys were annealed at different temperatures in order to simulate the exit condition of the alloys from hot rolling mills. Textures were determined by the normal pole figure method and low resolution technique which determines several texture components by X-ray diffraction. The empirical equations between the texture components determined by the low resolution technique and other texture components are derived. The on line R-value determination is simulated and the reliability is discussed.

3:00 PM
THE INFLUENCE OF PRE-HEAT TREATMENT ON THE RECRYSTALLIZATION AND TEXTURE OF STRIP CAST AA3004 ALUMINUM ALLOY: *Y. L. Liu*[1]; J. Qiu[1]; G. Liao[1]; J.G. Morris[1]; [1]University of Kentucky, Light Metals Research Laboratories, 177 Anderson Hall, Lexington, KY 40506 USA

The strip cast process provides a significant advantage for producing packaging materials. However, the metallurgical and mechanical characteristics of the material produced by the strip cast process are quite different from material produced by the traditional DC casting process. Therefore, it is of industrial interest to carry out further research on the strip cast material. In this study, the packaging material, aluminum alloy AA3004, was industrially produced by the strip cast process. The hot band was subjected to various heat treatments. The evolution of the microstructure and texture during heat treatment was examined. The influence of heat treatment on the recrystallization behavior and texture behavior of the cold rolled sheets was invested. The effect of pre-existing texture on the evolution of texture during annealing of the cold rolled sheets is discussed.

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DEFORMATION MICROSTRUCTURE AND SLIP PATTERN IN ALUMINUM: *N. Hansen*[1]; [1]Riso National Laboratory, Materials Research Dept., Rosklide DK-4000 Denmark

Aluminium and aluminium alloys have been deformed in tension, rolling and channel die compression over a large strain range and a temperature range from RT to 600ϒC. The structural evolution has been followed by applying semiautomatic and automatic SEM and TEM techniques and it has generally been observed both in single crystals and polycrystals that the structures are subdivided by deformation induced dislocation boundaries and high angle boundaries. These boundaries have different characteristics depending on materials and process parameters. Of importance is the crystallographic orientations of the crystals or the grains. This parameter has been studied for the different deformation modes and it has been found that links exist between microstructure and local crystallography and the macroscopic plastic behaviour. This has led to an analysis of the effect of the slip pattern on the microstructural evolution as a function of strain and temperature. Finally is discussed the effect of grain orientation and slip pattern on the dislocation density and the stored energy of relevance to the modelling of the mechanical and thermal behaviour of aluminium and aluminium alloys.

4:00 PM
THE KINETICS OF ISOTHERMAL β" AND β' FORMATION IN AlMgSi ALLOYS: *Jörgen van de Langkruis*[1]; Marcel S. Vossenberg[1]; Wilhelmus H. Kool[1]; Sybrand van der Zwaag[1]; [1]Delft University of

Technology, Laboratory of Materials Science, Rotterdamseweg 137, Delft, Zuid Holland 2628 AL The Netherlands

The mechanical properties during and after processing of AlMgSi alloys are strongly influenced by the state of the alloying elements in the alloy. Especially, the formation of Mg2Si β'-phase has an important effect on the extrudability and also on the mechanical properties after extrusion by binding solute Mg and Si. In this work DSC experiments on several commercial and laboratory AlMgSi grades are described. The DSC used is equipped with fast heating (500 K/min) and quenching (200 K/min) facilities. The samples were solutionised, precipitated to induce isothermal transformation into β' or β'', rapidly quenched and subjected to a DSC scan. The heat treatment cycle was entirely performed in the DSC, which strongly improves experimentation time and quality. The effect of the heat treatments on the size and location of the β' and β'' peaks was studied. For an AA6063 type alloy it was found that after precipitation at 458 K the size of the β'' peak decreased with precipitation time, which is correlated with the amount of β'' already precipitated. It was also found that with increasing precipitation time, using a scanning rate of 10 K/min, the location of the β''-peak shifted to lower temperatures, whereas with scanning rate 5 K/min only the peak size decreased and a peak shift was not observed. This is attributed to the retarding effect of nucleation on the transformation, which is significant at high scanning rates and low β'' contents. Isothermal β' and β'' phase transformation diagrams of some of the grades investigated are presented. Compositional effects were also observed: adding excess Mg, excess Si or Fe changes the size and location of the β' peak and tends to decrease the 50% β' transformation time. Also some precipitation peaks were observed, which do not occur in stoichiometric AlMgSi alloys.

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ODF ANALYSIS ON TEXTURE OF 3004 ALLOY SHEET: *Sachio Urayoshi*[1]; Ryou Shoji[1]; [1]The Furukawa Electric Co., Ltd., Material Engineering Section, 21-1 Kurome, Mikuni-cho, Sakai-gun, Fukui Prefecture 913-0048 Japan

The rolling texture of 3004 aluminum alloy was analyzed by examining its orientation distribution function (ODF). The aim was to study the difference texture resulting from two typical production methods for can body stock. First, the rolled materials were studied right after intermediate annealing; it was found that the material continuously annealed after being hot rolled (hereafter called HCAL) had a recrystallized texture with a high accumulation of the cube-orientation {001} <100>. However the material continuously annealed after being both hot rolled and cold rolled (hereafter called ICAL) had a lower cube-orientation accumulation than the HCAL material, and it showed a random recrystallized texture with little accumulation of any particular orientations. On the other hand, after final cold rolling, the HCAL material, with a high final reduction, exhibited a deviation in peak orientation density from the S orientation to the Brass orientation, and the ICAL material, with a low reduction, from the S orientation to the Cu orientation. In both cases, the peak orientation did not coincide with the S orientation which is characteristic of the rolling texture.

ALUMINUM REDUCTION TECHNOLOGY: Emerging Technologies

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

Wednesday PM Room: 6F
March 3, 1999 Location: Convention Center

Session Chairs: Jay Bruggeman, Alcoa Aluminium Company of America, Chem. Sys. Div., Alcoa Center, PA 15069-0001 USA; Barry Welch, The University of Auckland, Dept. of Chem. & Mats. Eng., Auckland 1001 New Zealand

2:00 PM

PATHS FOR ALUMINIUM PRODUCTION IN THE NEW MILLENNIUM: *B. J. Welch*[1]; [1]Auckland University, Dept. of Chemical and Materials Engineering, Private Bag 92019, Auckland New Zealand

In the last two decades we have seen the demise of the much heralded ASP Chloride Process as an alternative Aluminium metal production path, a drying up of papers on carbo-thermal production options, but a steady stream of articles proposing the use of drained cathode technology (by a wettable titanium diboride coating) and others extolling the virtues and potential materials for inert anode technology. We also saw a rush of smelter technologies papers in the early 1980's claiming energy consumption achievable less than 12.5 kWh per kg. However the recent emphasis has been on high amperage, more cost efficient technologies. Current efficiencies in excess of 96% can be routinely obtained by new technologies and even aged technologies can be retrofitted to perform at 95%. The challenge then is to lower cell voltages and one of the key limitations for this is the need to maintain adequate superheat while avoiding of sludge formation and electrolyte concentration gradients. Electrochemical technology based on the new concepts being considered (drained wetted cathodes, inert anodes, and even chloride electrolytes) face exactly the same problems and challenges that the present technology does but they are even more acute and demanding. These challenges can be met however and undoubtedly the industry is faced with interesting times as it continues to strive to be competitive.

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INERT ELECTRODES IN ALUMINIUM ELECTROLYSIS CELLS: *H. Kvande*[1]; [1]Hydro Aluminium Metal Products, P.O. Box 80, Stabekk N-1321 Norway

Inert electrodes would mean a technological revolution of the Hall-Héroult process. The production costs for aluminium may be reduced by 15 to 20% by avoiding the consumable carbon anodes, and by lowering the energy consumption by use of a wettable or drained cathode. Environmentally, all $C0_2$ and CF_4 gas emissions from the cells would be eliminated. Considerable progress has been achieved with respect to the development of wettable cathodes on the basis of titanium diboride. However, little or no success has been reported for inert anodes, and the development of an inert anode material has appeared to be extremely difficult. In spite of its high research priority, it is possible that a viable technological solution for an inert anode may not be found in the foreseeable future. The present paper reviews the state-of-the-art of inert anodes and cathodes in aluminium electrolysis cells, and discusses their main economical, technological and environmental advantages. Bipolar cells would be the superior cell construction, but these still represent a great challenge to researchers in the field of materials science.

3:05 PM

A DYNAMIC INERT METAL ANODE: *J. N. Hryn*[1]; M. J. Pellin[2]; [1]Argonne National Laboratory, Energy Systems Division, 9700 S. Cass Ave., Bldg. 362, Argonne, IL 60439 USA; [2]Argonne National Laboratory, Mats. Sci. Division, 9700 S. Cass Ave., Bldg. 200, Argonne, IL 60439 USA

A new concept for a stable anode for aluminum electrowinning is described. The anode consists of a cup-shaped metal alloy container filled with a molten salt that contains dissolved aluminum. The metal alloy can be any of a number of alloys, but it must contain aluminum as a secondary alloying metal. A possible alloy composition is copper with 5 to 15 weight percent aluminum. In the presence of oxygen, aluminum on the metal anode's exterior surface forms a continuous alumina film that is thick enough to protect the anode from chemical attack by cryolite during electrolysis and thin enough to maintain electrical conductivity. However, the alumina film is soluble in cryolite, so it must be regenerated in situ. Film regeneration is achieved by the transport of aluminum metal from the anode's molten salt interior through the metal wall to the anode's exterior surface, where the transported aluminum oxidizes to alumina in the presence of evolving oxygen to maintain the protective alumina film. Periodic addition of aluminum metal to the anode's interior keeps the aluminum activity in the molten salt at the desired level. This concept for an inert anode is viable as long as the amount of aluminum produced at the cathode greatly exceeds the amount of aluminum required to maintain the anode's protective film.

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REDUCTIONS CONDITIONS ENCOUNTERED IN CRYOLITE BATHS: *J. A. Sekhar*[1]; J. Liu[1]; H. Deng[1]; [1]University of Cincinnati, Dept. of Materials Science and Engineering, International Center for Micropyretic, P.O. Box 210012, Cincinnati, OH 45221 USA

We have noted an unusual effect that several of the oxide and ferrite materials which are being considered for use as non-consumable anodes are reduced by the bath to the metallic state when held for even short durations in the bath. Conditions for such reduction are explored. In addition, when reduced to metal, the product retains the shape and approximate dimensions of the initial oxide form. The implications of this effect on the utility as a non consumable anode are explored.

3:55 PM BREAK

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CHARACTERIZATION OF WETTABLE TiB2-CARBON MATERIAL COMPOSITE: *M. Dionne*[1]; A. Mirtchi[2]; G. L'Espérance[1]; [1]Centre for Characterization and Microscopy of Materials, Dept. of Metallurgical and Materials Engineering, Ecole Polytechnique de Montreal, P.O. Box 6079, Succ. Centreville, Montreal, Quebec H3C 3A7 Canada; [2]Alcan International, Ltd., Electrolysis, 1955, Mellon Blvd., Jonquiere, Quebec G7S 4K8 Canada

Since the continuous improvement of the conventional carbon cathode blocks over the years and the advantages of TiB_2 such as good wettability by liquid aluminum, relatively good electrical conductivity and wear resistance, it was an attractive idea to intimately mix those two giving birth to a wettable TiB_2-carbon material with totally new properties. In this presentation, the chemical stability of TiB_2 particles in molten aluminum and in the electrolytic bath is discussed. Results showing the characterization of TiB_2-carbon composite material after electrolysis and immersion tests are presented as well as results showing the dissolution of TiB_2 particles, by the electrolytic bath, along specific crystallographic planes. Furthermore, evidence that Al_2O_3 saturated electrolytic bath enhances dissolution of TiB_2 is presented.

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CATHODES WETTED BY ALUMINUM IMPROVE CURRENT EFFICIENCY: *W. Haupin*[1]; [1]2820 Seventh St. Rd., Lower Burrell, PA 15068 USA

The two major factors affecting current efficiency are bath chemistry and stability of the aluminum-bath interface. Bath chemistry sets the driving force at the aluminum-bath interface to transport dissolved metal into the bath where it becomes reoxidized. A stable aluminum-bath interface promotes a thick boundary layer that slows this transport. An unstable metal pad results from the motor action produced by horizontal currents in the aluminum interacting with the vertical magnetic field of the cell. Horizontal currents are caused primarily by undissolved alumina (muck) under the aluminum and to a degree by poor anode current balance. Muck forms in the bath filled capillary between the aluminum and the cathode (bottom of the cell). When the cathode is wetted by aluminum, there is no capillary and hence no place for muck to form and destabilize the cell. If cell design proceeds a step further to a wetted and drained cathode, the ultimate aluminum-bath interface stability is achieved and the maximum current efficiency for a given bath chemistry results.

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Al-Si CARBOTHERMAL REDUCTION USING HIGH-TEMPERATURE SOLAR PROCESS HEAT: *Jean P. Murray*[1]; [1]Colorado School of Mines, Engineering Division, Golden, CO 80401 USA

Aluminum production by carbothermal reduction is a very high-temperature, energy-intensive process. The temperature required, in the range 2300-2500K, is too high for practical process heat addition from combustion sources alone. Fuels must be burned in pure oxygen to reach 2000K, with very little process heat available, and combustion products present in the metal-forming zone interfere with the recovery of metal. Combustion-generated electricity contains only about a third of the energy in the fuel, and losses in the arc furnace cause further losses. Highly concentrated sunlight is capable of supplying adequate process heat at high temperatures. Alcoa researched and patented a carbothermal reduction process to make an Al-Si alloy suitable for further refining to pure aluminum or for use directly as an alloy. This process has been adapted to accept solar process heat and has undergone preliminary testing in a solar furnace.

5:15 PM

INVESTIGATION OF THE CONCENTRATION OF IMPURITIES FROM THE INERT ANODES IN THE BATH AND METAL DURING ALUMINIUM ELECTROLYSIS: *S. Pietrzyk*[1]; R. Oblakowski[1]; [1]University of Mining and Metallurgy, Dept. of Metallurgy Faculty of Non-Ferrous Metals, Al. Mickiewicza 30, Krakow 30-059 Poland

Three types of anodes: NiO-Fe_2O_3-CuO, NiO-Fe_2O_3-Cu, Cr_2O_3-NiO-CuO, were presented as candidates for inert anodes in Hall-Heroult process. The anodic behavior of anodes was studied during the electrolysis of Al_2O_3 in the 2,7 NaF,AlF_3 melt at 980ŶC. Inert anodes are subjects of simple mass transport controlled chemical dissolution into the electrolyte with subsequent transfer to cathodic metal surface where they are being reduced and dissolved into aluminium. The purpose of the present paper is to determine the factor governing the rates of anode dissolution and contamination of aluminium product.

CAST SHOP TECHNOLOGY: Cast House Safety

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

Wednesday PM Room: 6C
March 3, 1999 Location: Convention Center

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

2:00 PM

THE ALUMINUM ASSOCIATION'S MOLTEN METAL SAFETY PROGRAM: *Seymour G. Epstein*[1]; [1]The Aluminum Association, Inc., 900 19th Street, NW, Washington, DC 20006 USA

The aluminum industry has made an extensive effort to gain an understanding of molten metal explosions, the conditions under which they occur, and how they may be prevented. The Aluminum Association, the organization that represents the aluminum industry in the United States, has long considered the handling of molten aluminum its single greatest safety priority and has established an ongoing molten metal safety program to address the issues. The program includes research into the causes and prevention of molten aluminum water explosions; development and dissemination of guidelines for handling molten aluminum, for scrap receiving and inspection, and for sow casting and charging; a molten metal incident reporting program; a scrap rejection notification program; testing of fabrics to protect employees exposed to molten metal and pot bath; and a series of workshops, presentations and training aids to increase awareness. These will be discussed in the presentation.

2:25 PM

REDUCTION OF SOW DRYING CYCLE TIME USING MATHEMATICAL MODELING AND EXPERIMENTAL CONFIRMATION TESTS: *A. Giron*[1]; R. T. Richter[1]; [1]Aluminum Company of America, Alcoa Technical Center, Alcoa Center, PA 15069 USA

One of the most potentially dangerous cast house practices can be the charging of sows into molten metal that have not been dried or have been insufficiently dried. Aluminum sows can contain large shrinkage cavities which will very often be partially or completely filled with water. Several explosions causing severe burns, massive equipment damage and even fatalities have resulted when sows containing water were charged into molten metal. Alcoa, like other companies, have used very conservative sow drying practices to insure the moisture has completely evaporated from these shrinkage cavities. This, however, has caused production constraints due to limited drying furnace capacity. A program was undertaken using mathematical modeling supported by experimental testing to establish reduced, but still conservative, drying times for 1500 lbs. sows.

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INVESTIGATION OF COATINGS WHICH PREVENT MOLTEN ALUMINUM/WATER EXPLOSIONS: *D. D. Leon*[1]; R. T. Richter[1]; T. L. Levendusky[1]; [1]Aluminum Company of America, Alcoa Technical Center, Alcoa Center, PA 15069 USA

The Aluminum Association contracted Alcoa in 1995 to identify and test new protective coatings for casting pits as a replacement for Porter International's 7001 (Tarset Standard). Three new coatings have been identified through a series of selection criteria including: 1) An industry standard molten metal explosion test, 2) A multiple exposure test to measure durability, and 3) An external shock impact test. The results of this program will be reviewed. This study only tested protective coatings at the "in service cure time", as defined by the manufacturer. These curing times can be excessive for a production casting facility. The Aluminum Association has contracted Alcoa in a second program to investigate the effect of reduced cure times on coating adhesion and their effectiveness in preventing molten metal/water explosions. A status update of this new two year program is provided.

3:15 PM BREAK

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FUNDAMENTAL STUDIES ON MOLTEN ALUMINUM-WATER EXPLOSION TRIGGERING IN CASTING PITS: *Rusi P. Taleyarkhan*[1]; S. H. Kim[1]; [1]Oak Ridge National Laboratory, Engineering Technology Division, Bldg. 9204-1, MS 8045, Oak Ridge, TN 37831-8045 USA

Oak Ridge National Laboratory (ORNL) is conducting research on understanding fundamentals of molten metal-water explosion prevention with the Aluminum Association (AA). Phenomenological issues related to surface wettability, gas generation from coatings, charring of coatings, external shocks, melt/water temperature, inertial constraint, etc. are being investigated systematically to gage their relative impact on triggerability of surface assisted explosions. The Steam Explosion Triggering Studies (SETS) facility was designed and constructed to cost-effectively and safely address these issues. Hundreds of tests have been conducted to assess the viability of this approach to predict onset of explosion triggering. Uncoated surfaces included stainless and carbon steels, rusted steel, aluminum and concrete. Coatings tested included lime, silicone paint, graphite pain, greases, various coal tar epoxies, solid epoxies and epoxy mastics. Tests were also conducted to assess the impact of durability and bare spots. Data from studies with SETS facility were compared against field data taken over the past 50 years with excellent (100% correlation) results. The full paper will describe details of results of testing over coated and uncoated surfaces. Also described in the full paper will be a description of on-going work related to theoretical modeling, and future work dealing with addressing key issues related to impact of curing time, and field validation experiments of a novel prevention technique based on intentional gas injection at vulnerable locations.

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WILL AUTOMATION MAKE YOUR ALUMINUM CASTHOUSE A SAFER PLACE TO WORK?: *John E. Jacoby*[1]; [1]Consultant, 3398 North Hills Rd., Murrysville, PA 15668 USA

Techniques have been developed to start, run and complete drops of rectangular aluminum ingot cast by the DC, EMC and LHC processes without having personnel on the casthouse floor exposed to the hazards of molten aluminum explosions. During the entire cast all personnel are in a protected control room observing the cast on monitors. No operator intervention is required to start or end a drop. Do these automation systems improve casthouse safety and productivity? Answers to these important questions will be provided.

4:25 PM PANEL DISCUSSION

CAST SHOP TECHNOLOGY: Continuous Casting / Commercial Casting

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

Wednesday PM Room: 6D
March 3, 1999 Location: Convention Center

Session Chair: Dr. Jerry Dassel, Commonwealth Aluminum Corp., Uhrichville, OH 42351 USA

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HEAT TRANSFER IN THE SINGLE-ROLL STRIP CASTING PROCESS: *E. N. Straatsma*[1]; L. Katgerman[1]; W. H. Kool[1]; [1]Delft University of Technology, Laboratory of Materials Science, Rotterdamseweg 137, Delft, Zuid Holland 26 28 AL The Netherlands

In this research the influences of process parameters on the quality of 1 mm strip has been determined. Casting with a vertical feeding system is not recommended because of introducing turbulences resulting in bad strip quality. The quality can be classified with micrographs, roughness measurements and with thickness determinations. The stripcast process can also be simulated to determine the heat transfer coefficient between strip and wheel. The heat transfer coefficient between substrate and strip is one of the most important facts which influences the solidification rate. The determination of the heat transfer coefficient is very difficult and most of the simulation models assume values in a range of 8-20 kW/m2K. We are able to determine the heat transfer coefficient by online temperature measurements in the wheel of a single roll strip caster at laboratory scale. Together with the continuous measurement of the final strip temperature it is possible to compute the heat transfer coefficient.

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STRIP CASTING OF ALUMINIUM USING TWIN ROLL CASTERS: *Manish Gupta*[1]; Dan P. Cook[2]; Yogeshwar Sahai[1]; [1]The Ohio State University, Mats. Sci. & Eng., 477 Watts Hall, 2041 College Rd., Columbus, OH 43210 USA; [2]Reynolds Metal Company, Corporate Research and Development, Richmond, VA 23219 USA

Twin roll casters are the most commonly used machines for strip casting of aluminium. These casters offer low investments and very high operational flexibility. In the present work, turbulent fluid flow, heat transfer and solidification during strip casting of aluminium by twin roll caster was simulated by a two-dimensional finite element model. From this model, roller speed, contact angle, gap heat transfer coefficient and melt super heat were identified as important process variables which affect the thickness of cast strip. The model also predicts velocity and temperature profile in melt pool and the roller. Effect of angle of injection of molten metal into melt pool on the process was also studied. From the present study, roller speed, contact angle and gap heat transfer coefficient were found to be the main parameters affecting the strip thickness. Cooling fluid temperature, melt superheat, roller thickness and roller material were found to have little effect. Applicability of this mathematical model in industrial production of aluminium strips was also verified.

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TWIN ROLL CASTING OF ALUMINUM AT 2.5 MM GAUGE - PRODUCTION EXPERIENCE AND PROCESS IMPROVEMENTS: *S. Hamer*[1]; D. Smith[1]; B. Taraglio[1]; C. Romanowski[1]; [1]Fata Hunter, 6147 River Crest Dr., P.O. Box 5677, Riverside, CA 92507 USA

Assan Demir Sac Sanayi A.S. in Turkey has now purchased four FATA Hunter SpeedCaster machines. The first of these machines was commissioned two years ago and has been casting 2.5 mm thick aluminum strip on a production basis for almost one European and Near East markets. To achieve stable and high quality production, some of the equipment and casting parameters required optimization. This paper describes these process improvements together with the resulting production rates and cast strip properties. This long-term operation has also revealed some aspects of the process which needed further refinement. Development programs which addressed these issues and plans for further down gauging are briefly reviewed. The operational experience gained has been incorporated into the next generation of casting line automation systems. Key features of these new automation systems are highlighted.

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COMMONWEALTH ALUMINUM -STATE OF THE ART CONTINUOUS CASTING: *Stan Platek*[1]; [1]Commonwealth Aluminum, 7319 Newport R., SE, Uhrichsville, OH 44683 USA

The operating experience of Commonwealth Aluminum in continuous strip casting spans over twenty years and four Hazelett twin belt casters. Billions of pounds of strip have been cast in widths ranging from 12-52 inches. Alloy and production capabilities have been dramatically expanded in recent years by virtue of improved casting belt surfaces, magnetic caster mold stabilization techniques and new and improved metal feeding systems. Improved belt surfaces provide a more consistent and higher level of cast slab surface quality. Powerful magnetic means constrain the casting belts from thermal distortion providing an opportunity to employ a greater range of cooling rates for specific alloys. The use of unique closed pool feeding nozzles employing a combination of refractories and metals reveals the subtle effects of metal flow on surface metallurgy. The chronology of the emergence of Commonwealth continuous cast product into the aluminum sheet mainstream is presented along with a detailed review of the most current technologies employed and the resulting metallurgy and product.

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CASTEX CONTINUOUS BAR CASTING FOR THE NEXT MILLENNIUM:B. Maddock[1]; P.M. Thomas[1]; R. Wilkinson[1]; [1]Holton Conform Ltd., United Kingdom

Over the past decade a number of changes have occurred in the production of aluminum strip products. There has been a general trend towards downgauging and a move toward true mini-mills. If the production of feedstock for products other than strip is examined, it is clear that the same logic can be applied to these processes. The number of process operations can be reduced with the cast gauge/cross section much closer to that of the finished product. Most of the feedstock for extrusions and wire and rod products is produced either by traditional billet casting or by wheel and belt casters and in both cases, considerable downstream equipment is required, and the productivity requirements for economic production high. Conform is an established technology for the production of a variety of extrusions and rod and wire products and is capable of processing a number of different feedstocks. The feedstock can be bar that is continuously cast immediately prior to the Conform machine and there is the potential for using molten metal as the feedstock. The paper will describe a Castex installation where continuously cast feedstock is produced and the results and process issues will be discussed. In addition, an experimental facility to evaluate direct liquid metal feed will be described.

4:05 PM BREAK

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A GENERAL APPROACH FOR DETERMINATION OF RELEASE DIRECTIONS FOR DIECASTINGS: *Lu Hongyuan Lu*[1]; W. B. Lee[1]; [1]Hong Kong Polytechnic University, Manufacturing Engineering, Hung Hom, Kowloon, Hong Kong China

In design of diecasting dies, the determination of parting surface is particularly important and heavily depends on the individual experience of designer. In order to assist design automation of diecast die, a computer-aided approach is presented for choice of parting direction and parting surface based on the geometry features. According to the translation principle of a rigid body, all candidate parting directions (CPD are solved out. A CPD distribution order is used for evaluating the priority of each CPD acting as parting direction in removability. Then a preferred parting direction and parting surface can be determined. The geometry features are extracted by sweeping the shape of cast component to be cast. The CPD distribution order is obtained by finding the intersection of removable direction polygons.

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AN EXPERIMENTAL AND COMPUTATIONAL EVALUATION OF THE INFLUENCE OF PERMANENT MOULD DESIGN ON THE SOLIDIFICATION OF Al7SiMg CASTINGS: *John Anthony Spittle*[1]; Stephen G. R. Brown[1]; Hannelore Wishart[1]; [1]University of Wales Swansea, IRC in Materials for High Performance Applications, Singleton Park, Swansea SA2 8PP UK

An experimental permanent mould, for Al7SiMg alloy castings having a tensile test specimen geometry, has been used to assess the influence of mould geometry and water cooling on the steady-state temperature distribution in the mould and the macro-freezing pattern of the casting. From observation, a steady-state was assumed to be achieved in any batch run after 20 castings. The temperature distribution was derived from thermocouples located in the mould and was compared with the distribution predicted by the MAVIS heat transfer/solidification simulation package. The freezing pattern was experimentally evaluated, from the variation in secondary dendrite arm spacing in the casting, and was compared with the macrofreezing pattern predicted by MAVIS. It was found that mould sculpting, casting fins and mould water cooling had little influence on the freezing pattern which was dominated by the casting geometry.

5:05 PM

INFLUENCE OF MOLD COATING PROPERTIES ON ALUMINUM ALLOY CENTRIFUGAL CASTINGS: *Kevin Gilbert Cook*[1]; Ramana G. Reddy[1]; [1]The University of Alabama, Metall. and Mats. Eng., P.O. Box 870202, Tuscaloosa, AL 35487-0202 USA

Tubular Al-Si parts were produced using a permanent mold horizontal centrifugal caster. The effects of mold coating, rotation speed, and mold temperature on the casting micro and macrostructures were evaluated. Permeabilities of boron nitride, graphite, bentonite, and alumina coatings were measured using a modified green sand perimeter. The coatings were applied to the cylindrical low carbon steel mold and preheated before pouring the molten metal. Mold preheating temperatures were varied from 50-250ŸC (122-482ŸF). The cast products were examined for surface and structural defects, and the samples were sectioned

and analyzed using optical microscopy, scanning electron microscopy, and x-ray diffraction. Results showed that element distribution in the cast structure is strongly dependent on rotation speed. Typically, higher mold temperatures and high permeability coatings produced better casting structures. Heat transfer coefficients were also calculated for the corresponding coating systems.

CREEP BEHAVIOR OF ADVANCED MATERIALS FOR THE 21ST CENTURY: Low Stress Creep Mechanisms: A Discussion II

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

Wednesday PM Room: 15A
March 3, 1999 Location: Convention Center

Session Chair: A. K. Mukherjee, University of Canifornia, Davis, CA 95616 USA; T.R. Bieler, Michigan State University, East Lansing, MI 48824-1226 USA

2:00 PM BREAK

2:10 PM INVITED PAPER
QUANTITATIVE PREDICTIONS OF THE DISLOCATION NETWORK THEORY OF HARPER-DORN CREEP: *Alan J. Ardell*[1]; Marek Przystupa[1]; [1]University of California, UCLA, Dept. of Materials Science & Engineering, 6531-G BH, Los Angeles, CA 90095 USA

It has been demonstrated that the dislocation network theory of high-temperature deformation is capable of explaining many features of Harper-Dorn (H-D) creep. The observation that the dislocation density in the H-D creep regime is independent of the applied stress is explained by the frustration of dislocation network coarsening, which arises because of the exhaustion of Burgers vectors that can satisfy Frank's rule at the nodes in the network. The theory also accounts for the dramatic reduction in the steady-state creep rate that obtains when the initial dislocation density is very large, for example in specimens deformed by cold-working prior to creep testing. Other characteristics of H-D creep, such as the transition stress from H-D to power-law creep and the reduction in the dislocation density during primary creep in the H-D regime, are also satisfactorily explained. No other theory of H-D creep can account for the totality of these experimental observations. In this work we attempt to solve the equations of the network theory in order to provide a quantitative description of the experimentally measured distributions of dislocation link lengths in Al, and a self-consistent description of creep curves in Al deformed in the H-D regime.

2:35 PM INVITED PAPER
DIFFUSION CREEP IN CERAMICS: *Atul H. Chokshi*[1]; [1]Indian Institute of Science, Department of Metallurgy, Bangalore 560 012 India

At sufficiently low stresses, where intragranular dislocation mobility is rather limited, plastic deformation can occur solely by the diffusion of vacancies either through the matrix (Nabarro-Herring) or along grain boundaries (Coble). The process of diffusion creep has been modeled theoretically for over 50 years now, although there still remain some doubts over the experimental validation of the models. It has been suggested that low intragranular dislocation mobility leads to more frequent observations of diffusion creep in ceramics compared to metals. In ceramics, the diffusion creep process is more complex than in metals due to the need to account for charge balance and the transport of two or more ionic species along two different paths (lattice or grain boundary). The present report will evaluate critically the experimental observations of diffusion creep in some oxide-based ceramic systems. In addition, the process of ambipolar diffusion in ceramics will be examined with two different considerations: (a) the total flux to grain boundaries is in the appropriate stoichiometric ratio, so that the cations and anions may be transported along different paths, and (b) the flux along each transport path is in the appropriate stoichiometric ratio. It will be demonstrated that the above two considerations lead to substantially different predictions on rate controlling processes.

3:00 PM
DIFFUSIONAL CREEP AND HARPER-DORN CREEP AT INTERMEDIATE TEMPERATURES: *Lubos Kloc*[1]; Jaroslav Fiala[1]; Josef Cadek[1]; [1]Academy of Sciences of the Czech Republic, Institute of Physics of Materials, Zizkova 22, Brno CZ-61662 Czech Republic

Viscous creep was observed at temperatures close to one half of absolute melting point at very low creep rates in many materials. The results were interpreted as Coble diffusional creep and/or Harper-Dorn dislocation creep. Some of the results are in very good agreement with the Coble theory of diffusional creep and can support the diffusional creep as an important deformation mechanism under certain conditions. Nevertheless, the theory of diffusional creep seems to be too simplified to describe accurately the diffusional creep processes. In several materials, dependence of the creep rate on grain size corresponds to Coble diffusional creep for grain sizes below approximately 100 μm, while this dependence is replaced by large data scatter for coarse grain sizes. This behaviour used to be interprete as a transition from diffusional to Harper-Dorn creep regime. The structural parameter responsible for the large scatter of creep rates at large grain sizes has not been identified yet.

3:20 PM
EXPERIMENTAL STUDIES OF CREEP PHENOMENA AT LOW STRESSES: *K. R. McNee*[1]; Howard Jones[1]; [1]University of Sheffield, Dept. Engineering Materials, Mappin Street, Sheffield S1 3JD UK

Some creep formulations indicate a continuity of relationships throughout large ranges of stress and temperature. Other evidence has also been presented indicating distinct regimes each representing the predominance of a specific deformation mechanism. In low stress creep the theory is well established to indicate that directional diffusion has an important role and provides a quantitative dependence of creep rate on measurable parameters. Experiments are described which provide evidence of the stress, temperature and grain size dependence of creep which, in combination with microstructural observations, provides clear support for the occurrence of diffusional creep processes.

3:40 PM
PRIMARY CREEP OF METALLIC MATERIALS AT LOW STRESSES AND INTERMEDIATE TEMPERATURES: *Lubos Kloc*[1]; Vaclav Sklenicka[1]; [1]Academy of Sciences of the Czech Republic, Institute of Physics of Materials, Zizkova 22, Brno CZ-61662 Czech Republic

Some creep mechanisms acting at low stresses have not their own primary stage. Nevertheless, the primary creep has been observed in almost all low stress creep experiments. Hence, special primary creep mechanisms must be responsible for primary creep under such loading conditions. Better understanding of these mechanisms seems to be important for engineering practice, because the overall strain allowed for some components in high temperature technology may be essentially exhausted by primary creep. The primary creep parameters like primary strain, the duration of primary creep stage, initial creep rate and initial to secondary creep rate ratio are analyzed for several metallic materials from pure metals to heat-resistant steel. It can be concluded, that no mechanism proposed till now for primary creep at low stresses is capable to explain all observed features of primary creep under given conditions.

4:00 PM
PRIMARY CREEP AND ANELASTICITY AT LOW STRESSES: *R. S. Mishra*[1]; A. K. Mukherjee[1]; [1]University of California, Department of Chemical Engineering and Materials Science, One Shields Avenue, Davis, CA 95616 USA

At low stresses, three deformation mechanisms are dominant; diffusional flow, grain boundary sliding and viscous dislocation creep. The relative contribution is governed by the grain size and temperature. The magnitude of primary creep is often significantly higher than that predicted by theoretical or phenomenological models for these mechanisms. Some anelasticity results show that the primary creep at low stresses is fully recoverable. This raises doubts about the applicability of previous models for primary creep at low stresses. The advantages of anelasticity studies for understanding of low stress creep mechanism are discussed.

4:20 PM DISCUSSION ON LOW STRESS CREEP MECHANISMS

ELECTRICAL AND THERMAL PROPERTIES OF MATERIALS: Session II

Sponsored by: Electronic, Magnetic & Photonic Materials Division, Electronic Packaging and Interconnection Materials Committee
Program Organizers: Sungho Jin, Lucent Technologies, Bell Labs, Murray Hill, NJ 07974 USA; Anthony Mulligan, Advanced Ceramics Research, 851 East 47th St., Tuscon, AZ USA; King Ning Tu, University of California, Dept. of Mats., Sci. & Eng., Los Angeles, CA 90095 USA

Wednesday PM Room: 16B
March 3, 1999 Location: Convention Center

Session Chair: S. Jin, Bell Laboratories, Lucent Technologies, Murray Hill, NJ 07974 USA

2:00 PM INVITED PAPER
HEAT CAPACITY, PHONONS, AND VIBRATIONAL ENTROPY OF NANOCRYSTALS: *B. Fultz*[1]; H. Frase[1]; J. L. Robertson[2]; [1]California Institute of Technology, Mail 138-78, Pasadena, CA 91125 USA; [2]Oak Ridge National Laboratory, Mail 6393, P.O. Box 2008, Oak Ridge, TN 37831 USA

The vibrational entropy and the heat capacity of a solid are determined primarily by its "phonon density of states DOS." This spectrum of interatomic vibrations is altered considerably when crystallites are 10 nm or smaller. From measurements by inelastic neutron scattering on Ni_3Fe [Phys. Rev. B57, 898 (1998)], we have identified two significant changes in the phonon DOS of nanocrystals: 1) an enhancement in the number of vibrational modes at low energies, and 2) a broadening of features in the phonon DOS, especially at high energies. The extra low energy modes can be attributed to the density of grain boundaries in this material. The broadening of the DOS at high energies can be changed independently of the grain size. We present evidence that this broadening is sensitive to the internal structure of grain boundaries. These two alterations of the phonon DOS change considerably the vibrational entropy of nanocrystalline materials, although they do so in opposing ways.

2:30 PM INVITED PAPER
FIBER-TYPE MMCS FOR ELECTRONICS THERMAL MANAGEMENT: *S. Shiga*[1]; J. Ninomiya[1]; A. Hideno[1]; K. Mihara[1]; Y. Oyama[1]; [1]Furukawa Electric Co., Ltd., Metal Research Center, R&D Div., 500 Kiyotaki, Nikko 321-0942 Japan

High thermal conductivity materials along with tailored coeffecients of thermal expansion (CTE) are still in the developing area of materials and industrial technology. High thermal conductivity ceramics and powder-metallurgy-processed metal matrix composites (MMCs) are both commercially used. They are mostly non-directional in thermal performance. Two types of fiber-containing MMCs (FRM) were developed for industrial applications. Their usefulness was demonstrated in terms of the nature of the FRMs; 1) High thermal conductivity carbon fiber/Al or Cu composites exhibit the maximized thermal performance in one-/or two-dimensional orientation along the fiber length. In the case of the two-dimensional orientation, the conductivity in the x-y plane doubles that in the y-axis while keeping the CTE tailored. 2) Cr-fiber/Cu MMCs in which fine Cr-fibers are in-situ incorporated in high-purity Cu matrix, show thermal conductivity values comparable to that of Cu, and CTE values comparable to those of glass ceramics and plastic packaging materials. The thermal properties of these composites appear to be independent of fiber directionality. The material property characterization and some examples of applications will be presented.

3:00 PM INVITED PAPER
CONTROL OF THERMAL EXPANSION BEHAVIOR IN ELECTRONIC MATERIALS: *S. Jin*[1]; H. Mavoori[1]; [1]Bell Laboratories, Lucent Technologies, 600 Mountain Ave., Murray Hill, NJ 07974 USA

Thermal expansion behavior of materials, especially the mismatch in the coeffecient of thermal expansion (CTE) among various component materials in electronic devices and packages, is an important issue in terms of device performance and reliability. The CTE is generally considered to be an intrinsic property of materials. However, there are some novel ways of modifying the thermal expansion behavior, e.g., so as to obtain very small, very large, near-zero, or negative CTE values by utilizing magnetic transition or phase transition near room temperature. Some examples of CTE control in electronic materials and composite structures, as well as their potential device applications will be discussed.

3:30 PM BREAK

3:50 PM INVITED PAPER
INCREASING THE THERMAL CONDUCTIVITY OF BORON NITRIDE AND ALUMINUM NITRIDE PARTICLE EPOXY-MATRIX COMPOSITES BY PARTICLE SURFACE TREATMENTS: Yunsheng Xu[1]; *Deborah D. L. Chung*[1]; [1]State University of New York at Buffalo, Dept. of Mech. & Aero. Engr., 608 Furnas Hall, Amherst, NY 14260 USA

The thermal conductivity of boron nitride and aluminum nitride particle epoxy-matrix composites was increased by up to 97% by surface treatment of the particles prior to composite fabrication. The increase in thermal conductivity is due to decrease in the filler-matrix thermal contact resistance through the improvement of the interface between matrix and particles. Effective treatments for BN involved acetone, acids (nitric and sulfuric) and silane. The most effective treatment involved silane such that the coating resulted from the treatment amounted to 2.4% of the weight of the treated BN; less coating was less effective. The effectiveness of a treatment was higher for a larger BN volume fraction. At 57 vol.%, the thermal conductivity reached 10.3 W/m.C. The treatment had little effect on the specific surface area of the BN particles. Silane treatments were also effective for AlN. At 60 vol.% AlN, the thermal conductivity reached 11 W/m.c.

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THERMAL CONTACT CONDUCTANCE STUDIED BY TRANSIENT LASER FLASH METHOD: Xiangcheng Luo[2]; *Deborah D. L. Chung*[1]; [1]State University of New York at Buffalo, Dept. of Mech. & Aero. Engr., 608 Furnas Hall, Amherst, NY 14260 USA

The thermal contact conductance between two copper disks as well as between copper and silver epoxy was studied by transient laser flash method. The parameters, which have influence on the thermal contact conductance between copper disks, include compressive pressure applied between copper disks, surface roughness and surface treatment of copper disk surfaces. The higher the contact pressure, the higher thermal contact conductance and furthermore, the contact conductance between two copper disks with rough surface increases more rapidly with the increase of contact pressure than the one with smooth surfaces. A heat sink compound greatly increases the thermal contact conductance between copper disks. The thermal contact conductance between copper and silver epoxy can also be increased by acid washing of copper sur-

faces. Finite element program ABAQUS was used to calculate the thermal contact conductances through time vs. temperature curves which were obtained by experiment.

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THERMAL AND OPTICAL PROPERTIES OF POROUS ALUMINUM OXIDE: *Dennis W. Readey*[1]; Jesus Vazquez[1]; [1]Colorado School of Mines, Dept. of Metall., 1500 Illinois Ave., Golden, CO 80401 USA

The optical reflectivity of ceramic powders depends on the number of scattering interfaces per unit thickness and the optical absorption of the material itself. As sintering occurs, necks between particles reduce the reflective area between particles and, hence, the reflectivity. In contrast, the thermal conductivity of porous ceramics should increase as the interparticle contact area increases during sintering. Models and experiments of both optical reflectivity and thermal conductivity of Al2O3 are compared. Vapor phase sintering in HCl is used to produce increased grain size and interparticle contract without increasing density.

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ALUMINUM NITRIDE WITH HIGH THERMAL CONDUCTIVITY FROM ALUMINUM METAL COMPACTS: *T. Okada*[1]; M. Toriyama[2]; S. Kanzaki[2]; [1]Fine Ceramics Research Association, Nagoya 462-8510 Japan; [2]National Industrial Research Institute of Nagoya, Nagoya 462-8510 Japan

Aluminum nitride (AlN) with high thermal conductivity was synthesized by direct nitridation of a mixture of aluminum (Al) powder with 5 wt% of yttria, and followed by sintering at 2173K. To prevent changes in the compacts shape, before and after processing, nitridation was performed at nominal temperatures below the melting point of Al and nitrogen pressures 0.5-7 MPa. After nitridation, the generated AlN compacts reached 75-80% of the theoretical density. Densified over 95% of the theoretical density was achieved by sintering at 2173K for 4h in nitrogen atmosphere. The thermal conductivity of 170 W/mK was achieved by controlling the nitridation condition. The role of final oxygen concentration and nitridation conditions on the thermal performance is discussed.

FLUID-FLOW PHENOMENA IN METALS PROCESSING: Melting and Refining Processes

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

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

Session Chairs: David G.C. Robertson, University of Missouri-Rolla, Rolla, MO 65409-1460 USA; R. L. Guthrie, McGill University, Montreal, Quebec H3A 2A7 Canada

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SIMULATION OF IMPINGING JET APPARATUS FOR GAS-LIQUID REACTION RATE MEASUREMENT: *M. Philip Schwarz*[1]; [1]CSIRO Minerals, P.O. Box 312, Clayton South, Vic 3169 Australia

The rate of reaction of oxidizing gases with iron/carbon melts is of importance in direct ferrous smelting because the extent of back-reaction must be minimized in these processes. Several researchers, including those at Carnegie Mellon University (CMU), have measured rates for CO2 and H2O with an iron/carbon/sulphur melt using a small experimental reactor in which the gas jet impinges on the melt. Some attempts have been made to perform such an experiment with oxygen, but in this case it may not be possible to operate in the chemical kinetics limited regime because of the high rate of reaction of O2 at the surface. The interpretation of rate measurements in such cases could be assisted by Computational Fluid Dynamics (CFD) simulation in which both gas side mass transfer and chemical kinetics are taken into account. A CFD model for the gas-side of an impinging jet iron bath reactor has been developed to assist in the interpretation of such experiments and in their design. Heat transfer and reaction at the surface have been included. A free surface model, which solves for the liquid motion within the bath as well as the gas motion above the bath, has also been developed. This model also predicts extent and shape of the dimple formed on the liquid surface by the impinging jet. Both models have been run for conditions typical of jet impingement experiments using CO2, H2O and O2. The main conclusions are results from the model for gas-side mass transport are in good agreement with the empirical correlation of Belton and Belton (1980)· Experimentally determined rates of decarburization by CO2 should be corrected for mass transfer because the experiments are often carried out under mixed rate control, eg for gas flow rate 10 L/min when the sulphur concentration is lower than 0.045%. If the rate constant for oxygen reaction is greater than about 5 mol/m2.s.atm, it cannot be determined using a gas flow rate of 10 L/min or lower because of mass transfer control. A cavity of depth 4.5 mm is predicted for a gas flow rate of 10 L/min and this substantially changes the flow field compared with a simulation in which the surface is assumed to be flat. The predicted effective reaction rate can be much lower than expected when the cavity is so deep that the flow detaches from the bath surface at the lip of the cavity. This effect, if it actually occurs in the experiments, could bias measured rates.

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COMPARATIVE STUDY OF THREE CFD CODES IN MODELLING TWO-PHASE FLOW IN LADLE SYSTEMS: *J. Pitkala*[1]; J. L. Xia[1]; J. Vaarno[1]; [1]Helsinki University of Technology, Laboratory of Materials Processing and Powder Metallurgy, PB 6200, FIN-02015, HUT Finland

The present paper is to make a comparative study of three CFD codes in modelling the two phase flow in a water model ladle with central gas injection. The codes examined are CFX, Phoenics and Fluent. A Eulerian two phase model is used. Predictions are compared with experimental data available. Results show that the three codes can reasonably predict the gas-liquid plume in the ladle, and predictions are generally in a good agreement with experimental data. But differences do exist in predicting the gas volume fraction and velocity profiles. It appears that CFX gives the best prediction for the case considered.

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MODELLING THE MIXING OF LEAD BULLION DURING THE REFINING PROCESS.: *C. Bailey*[1]; K. Suman[1]; M. Patel[1]; T. Piper[2]; R. Forsdick[2]; [1]University of Greenwich, School of Computing and Mathematical Sciences, Wellington St., Woodwich, London SE18 6PF UK; [2]Britannia Refined Metals Ltd., Gravesend England

Lead bullion is mixed in kettles to remove a number of impurities including copper, silver, bismuth, etc. During the copper drossing process, lead ingots are melted and then mixed and cooled to a temperature where the copper plus a quantity of lead appears in a solid form (dross) at the liquid surface. Mixing is carried out using specific impeller designs, which form a vortex that ensures greater mixing of the dross. This results in finer dross, with a higher copper content, at the surface. To optimise this process it is important that vortex break-up does not occur at the impeller blades as this will oxidise the lead. This paper will present both water modelling (experimental) and computational fluid dynamic (mathematical) techniques currently being used to help understand this process. Validation of the mathematical models with water models and real plant data will also be presented.

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MELT REFINING: CFD MODELLING OF PARTICLE DEPOSITION TO GAS BUBBLES: *Knut Halvard Bech*[1]; *Stein Tore Johansen*[1]; [1]SINTEF, Materials Technology, Alfred Getz vei 2b, Trondheim N-7034 Norway

Removal of inclusion particles from melted aluminium can be facititated by means of a rotor system that supplies kinetic energy and gas to the floating metal. The surface of the gas bubbles collect particles as the bubbles rise from the point of gas injection to the surface, where the slagg can be removed. When applying computational fluid dymanics (CFD) to model such a system, one experiences difficulties with the large range of turbulent length-scales encoutered, from the large geometrical scales of the rotor and container, through the bubble size and down to the particle diameter. A mathematical model for the complete system is complex and require an extreme spatial resolution. Another way of dealing with the problem is to model the microscale phenomena separately and apply the results to create a model for the macroscopic system. The present work deals with turbulent particle flotation to idealized bubbles. Of the total turbulent kinetic energy generated by the rotor's work on the floating metal, only a fraction may contribute to enhanced flotation. By using a model spectrum for the turbulence, the fraction of turbulent energy in eddies smaller than the bubble diameter is calculated. A two-dimensional CFD model was then constructed to calculate the collision efficiency between particles and bubbles of various sizes. The results from the CFD parametric study were processed using multivariate analysis. The first principal component of the data set turned out to be the turbulent intensity, which is the ratio between the root-mean-square turbulent velocity and the rise velocity of the bubble. Another important finding was the if the bubble Reynolds number was too low, the collision efficiency decreased drastically. The bubble Reynolds number is proportional to the bubble size, which again is governed by the stirring power supplied to the rotor.

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THERMOPHYSICAL PROPERTIES FOR THE MODELLING FLUID AND HEAT FLOW IN HIGH TEMPERATURE PROCESSES: P. A. Day[1]; R. F. Brooks[1]; K. C. Mills[1]; *P. N. Quested*[1]; [1]National Physical Laboratory, Centre for Materials Measurement and Technology, Teddington, Middlesex TW11 0LW UK

Methods have been developed to provide reliable property data such as viscosity, density and surface tension for liquid commercial alloys required to describe fluid flow in high temperature processes. For viscosity, an oscillating viscometer was developed with a maximum temperature capability of 1650 degrees centigrade. Electromagnetic levitation techniques with a potential maximum temperature of 2000 degrees centigrade were developed for the measurement of density and surface tension. Changes in the frequency spectra during surface tension experiments will be discussed and are thought to be caused by the accumulation of oxide on the surface of the drop. Models have been applied to estimate these properties (and heat capacity and thermal conductivity) from the chemical composition of the alloy. The predicted results are compared with the experimental data.

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SURFACE PHENOMENA DURING SULPHUR INTERPHASE TRANSFER SLAG TO METAL: *Francisco Anastácio de Oliveira Neto*[1]; [1]Escola Politecnica da Universidade Federal da Bahia, Dept. Engenharia Hidraulica e Saneamento, Rua Aristides Novís, 2, Federação, Salvador 40210-630 Brazil

Interphase dispersion have been observed in presence of sulphur interphase transfer slag to metal at 1600ϒC. Possible mechanism given rise to these phenomena are analysed and discussed based upon recent published results of calcium aluminosilicate slag surface tension. Further insight into surface phenomena involving such melts during interphase mass transfer are highlighted. The results suggest a sulphur exchange mechanism which generates gas at the slag-metal interface and may also involve reduction of alumina. The reaction results in bubble nucleation at the slag-metal interface which leads to simultaneously dispersion of fine metal fragments into the slag by a fluid drag mechanism. It is possible that this effect will increase the overall reaction rates by increasing the effective interfacial area.

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ENTRAINMENT OF INCLUSIONS FROM THE DROSS IN STIRRED REACTORS FOR MELT TREATMENT: *Stein Tore Johansen*[1]; Svend Graadahl[1]; Thomas F. Hagelien[1]; [1]SINTEF, Materials Technology, Alfred Getz vei 2B, Trondheim, Trøndelag 7034 Norway

The dross appearing at the surface of an aluminium melt consists, in addition to aluminium, of mainly oxide films but also other non metallic inclusions. The inclusion particles are often poorly wetted by the metal and accumulate at the metal surface. However, in impeller stirred reactors for melt refining stirring may be exceedingly strong and inclusions accumulated at the metal surface may be entrained into the bulk metal. Concerning inclusion removal, such effects may deteriorate the effectiveness of melt refining. In this paper we investigate the surface entrainment of buoyant particles in a water model of an impeller stirred refining reactor. Under varying operating conditions the particle concentration in the bulk liquid is measured by laser light attenuation. The observed entrainment of particles is explained theoretically and metallurgical consequences of the findings are discussed.

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EFFECT OF FLUID FLOW ON INCLUSION COARSENING IN LOW ALLOY STEEL WELDS: *S. S. Babu*[1]; S. A. David[1]; T. Hong[2]; T. DebRoy[2]; [1]Oak Ridge National Laboratory, Metals and Ceramics Division, Oak Ridge, TN 37831 USA; [2]Pennsylvania State University, University Park, PA 16802 USA

Oxide inclusion forms in welds due to deoxidation reaction in the liquid steel. The inclusions control the weld microstructure development. Thermodynamic and kinetic calculation of oxidation reaction can describe inclusion characteristics such as number density, size, and composition. Experimental work has shown that fluid flow gradients in liquid weld pool can accelerate inclusion growth by collision and coalescence. Moreover, fluid flow in welds can transport inclusions to different temperature regions that may lead to repeated dissolution and growth of inclusions. The above phenomena are being studied with the help of computational coupled heat transfer - fluid flow - thermodynamic - kinetic models. The results show that the inclusion formation in steel welds can be described as a function of welding process, process parameters, and steel composition.

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A MATHEMATICAL MODEL FOR ESTIMATING THE EFFICIENCY OF CERAMIC FOAM FILTERS: F. A. Acosta-Gonzalez[1]; *A. H. Castillejos E.*[1]; [1]Centro De Investigacion y Estudios Avanzados del IPN, Unidad Saltillo, Apdo. Postal 663, Saltillo, Coahuila 25000 Mexico

Filtration as a terminal refining step for metals is widely used, particularly for the casting of aluminum alloys, but still more knowledge is required to understand how several factors affect the efficiency of removal of inclusions. In this study, both, initial and long term filtration efficiencies of ceramic foam filters have been comuted from the numerical solution of the two-dimensional Navier-Stokes equation and the motion equation for the solid particles, entering the pores of the filter. The complex structure of the foam filters is represented by a unit cell which is formed by a pair of pores with average structural parameters. The inlet boundary condition was defined from a physical model of the filter, which has similarity in Reynolds and Gravitational numbers. The fluid velocity measurements were done using particle image velocimetry (PIV); the measured and computed fluid flow fields showed good agreement. Also it was found, that the filtration efficiency depends strongly on the inclusions trajectory which is affected by the Reynolds, Gravitational and the Aspect Ratio numbers. High Gravitational numbers favors the collision of the particles with the wall increasing filtration efficiency. On the other hand, for low Gravitational numbers the particles follow the streamlines, avoiding contact with the wall and decreasing the filtration efficiency. Computed filtration efficiency values agree well with experimental measurements reported in the literature.

FLUID-FLOW PHENOMENA IN METALS PROCESSING: Solidification and Casting: Flow Processes

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

Program Organizers: Nagy El-Kaddah, University of Alabama, Dept. of Met. & Mats. Eng., Tuscaloosa, AL 35487-0202 USA; Stein Tore Johansen, SINTEF Materials Technology, Dept. of Proc. Metall.& 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

Wednesday PM Room: 5B
March 3, 1999 Location: Convention Center

Session Chairs: Chris Bailey, University of Greenwich, Center of Numerical Modeling and Process Analysis, Woolwich, London SE18 6pf UK; Haavard Thevik, SINTEF, Mats. Tech., Trondheim N-7034 Norway

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DYNAMIC BEHAVIOUR AND CONTROL OF MOLTEN METAL FLOW IN A COOLED PIPE: A. R. Firth[1]; *N. B. Gray*[1]; A. K. Kyllo[1]; B. N. McCurry[1]; [1]The University of Melbourne, Dept. of Chem. Eng., Parkville, VIC 3052 Australia

Dynamic control of the formation of a solidified layer between a pipe wall and a flowing melt enables the flow rate to be adjusted in real time. This solidified layer can be generated by using a coolant on the outside of a pipe wall to remove the required heat. The coolant and hence the solidified layer can be controlled remotely. The dynamic behaviour of the solidified layer is being investigated by both physical experiments and mathematical modelling. The experiments are being carried out using molten tin in a recirculating circuit and a cooling system that is instrumented for accurate computer control. The circuit is designed for flowrates up to 24kg/s (86 tph) of molten tin. A mathematical model has been developed using a finite difference technique to describe conduction through the pipe wall and solidified layer. A pseudo-first order time constant of 120s for a step change in an input variable is predicted by the mathematical model.

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MODELING HEAT TRANSFER AND FLUID FLOW IN GTA WELDING OF GAMMA TITANIUM ALUMINIDES: *Mario Arenas*[1]; Viola L. Acoff[1]; Nagy El-Kaddah[1]; [1]The University of Alabama, Metall. and Mats. Dept., P.O. Box 870202, Tuscaloosa, AL 35487 USA

A computational procedure to calculate heat and fluid flow in a stationary GTA weld pool is presented. Heat transfer and fluid flow in the molten pool can significantly influence such factors as the weld pool geometry, temperature gradients, local cooling rates and the solidification structure. The importance of liquid motion in a weld pool has been widely recognized recently. The present mathematical formulation considers buoyancy, electromagnetic, and surface tension as driving forces for the fluid motion. The problem is defined to be axially symmetric and transient to a steady state limit. The molten surface is flat. All thermophysical properties are constant. The numerical model was applied to a gamma titanium aluminide intermetallic alloy.

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FINITE ELEMENT MODELING OF MAGNETICALLY-DAMPED 3-D CONVECTION DURING SOLIDIFICATION: *Ben Q. Li*[1]; H. C. De Groh[2]; [1]Washington State University, School of Mechanical and Materials Engineering, Pullman, WA 99163 USA; [2]NASA Lewis Research Center, Cleveland, OH 44135 USA

A fully 3-D numerical model is developed to represent fluid instability and magnetic damping of complex fluid flow, heat transfer and electromagnetic field distributions in a melt cavity. The model is developed based on our in-house finite element code for the fluid flow, heat transfer and electromagnetic field calculations. The numerical model is tested against numerical and experimental results for water reported in literature. Various numerical simulations are carried out for the Sn-35.5% Pb melt convection and temperature distribution in a cylindrical cavity with and without the presence of a transverse magnetic field. Numerical results show that magnetic damping can be effectively applied to reduce turbulence and flow levels in the melt undergoing solidification and over a certain threshold value a higher magnetic field resulted in a higher velocity reduction. Also, a fully 3-D representation of the magnetic damping effects, the electric field induced in the melt by the applied DC magnetic field does not vanish, as some researchers suggested, and must be included even for molten metal and semiconductors. Furthermore, for the study of flow instability, a long enough time has to be applied to ensure the final fluid flow recirculation pattern.

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MODELING OF THE OXIDE FILM MOVEMENT, BREAKUP, AND ENTRAPMENT IN ALUMINUM CASTINGS: J. Lin[1]; *M. A. Sharif*[1]; J. L. Hill[1]; [1]The University of Alabama, Aerospace Engineering, P.O. Box 870280, Tuscaloosa, AL 35487-0280 USA

A numerical algorithm has been developed to simulate the movement, breakup, and entrapment of the oxide film inclusions encountered during the mold-filling processes of aluminum castings. The flowfield is solved using the well-known Marker and Cell (MAC) method by a time marching process. The Volume of Fraction (VOF) method is used to track the free surface boundaries. A kinematic approach is employed to track the movement and breakup of the oxide films on the free surface or in the bulk liquid metal. A series of computer simulations of two-dimensional mold-filling have been carried out. The computer program based on the proposed algorithm is able to model the flow behavior and oxide film movement, breakup, and entrapment in mold cavities for aluminum castings. The predictions are in good agreement with the experiments of other researchers.

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EXPERIMENTS AND COMPUTATIONS ON MOULD FILLING OF HORIZONTAL THIN-WALL CASTINGS.: *Robert van Tol*[1]; Laurens Katgerman[1]; Harrie Vanden Akker[2]; [1]Delft University of Technology, Laboratory of Metallurgy, Rotterdamseweg 137, Delft, Zuid-Holland 2628 AL The Netherlands; [2]Delft University of Technology, Kramers Laboratorium, Prins Bernhardlaan 6, Delft, Zuid Holland 2628 BW The Netherlands

Mould fillings of horizontal thin-wall castings have been captured using video-taping, contact measurements and thermo-couples. Additional to these measurements in actual castings, the integral velocity field has been measured in a water model, using particle image velocimetry (PIV). Together, these techniques reveal the displacement of the free surface, local temperatures and the velocity field during mould filling. Computer simulations have been performed, incorporating free surface flow with surface tension, heat transfer and solidification. A penetration theory based heat transfer coefficient at the metal mould interface was used, to prevent cell size dependence of the heat transferred on a mould filling time scale. Computational results show free surface shapes and velocity fields similar to experiments. Cold runs during mould filling can be predicted, using a criterion for the pressure at the ingot.

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AN INVESTIGATION OF HEAT TRANSFER RATES FOR MOLTEN DROPLETS FALLING IN A STAGNANT GAS: *J. Barry Wiskel*[1]; *Hani Henein*[1]; [1]University of Alberta, AM&PL, 536 Chemical-Mineral Bldg., Edmonton, Alberta T6G 2G6 Canada

A study was conducted to establish the effective heat transfer coefficient for a single molten droplet moving in a gaseous medium. Towards

this objective, a series of quench experiments were performed on molten droplets of AA6061 aluminum generated with the Impulse Atomization technique (IAP). IAP is a single fluid atomization process capable of producing powders with a predictable mean particle size and a relatively tight standard deviation under controlled atmospheric conditions. Microstructural analysis of the atomized powder was used to establish the extent of pre-quench solidification. A mathematical model was then employed to correlate the Ranz-Marshall and Whitaker equations with the observed particle cooling behaviour. These equations were found to provide a reasonable estimation of the heat transfer conditions only when the variation in gas thermophysical properties across the boundary layer were accounted for in the model. This model formulation of droplet heat transfer has important implications with regards to active spray and atomization processing operations.

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LIQUID PERMEABILITY MEASUREMENTS IN SOLIDIFYING ALUMINUM ALLOYS: A. J. Duncan[1]; Q. Han[1]; *S. Viswanathan*[1]; [1]Oak Ridge National Laboratory, Metals and Ceramics Division, Bldg. 4508, MS 6083, Oak Ridge, TN 37831-6083 USA

Measurements of liquid permeability in the mushy zones of Al-Cu and Al-Si alloy samples have been performed isothermally just above the eutectic temperature, using eutectic liquid as the fluid. A modified method has been developed to determine the specific permeability, K_S, as a function of time during the test from the data collected on these alloys. Factors affecting permeability measurements are discussed. Permeabilties are observed to vary throughout the experiment. This is attributed to microstructural coarsening and channeling that occurs in the sample during the experiment. The permeability is related to the microstructure of the sample using the Kozeny-Carman equation. The correlation between the measured K_S, liquid fraction, g_L and the specific solid surface area, S_V, improves markedly when compared to results from previous studies in which microstructural coarsening was ignored.

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THE ESTIMATION OF THERMAL RESISTANCE AT VARIOUS INTERFACES: *Stavros A. Argyropoulos*[1]; Norman J. Goudie[2]; Michael Trovant[3]; [1]University of Toronto, Dept. of Metall. and Mats. Sci., Walberg Bldg., Room 142, 184 College St., Toronto, Ontario M5S 3E4 Canada; [2]Bethlehem Steel Corporation, Home Research Laboratories, Bethlehem, PA 18016 USA; [3]Hatch Associates Ltd., Mississauga, Ontario L5K 2R7 Canada

Experimental and computational techniques were devised for the estimation of thermal resistance at various interfaces. Interfaces such as metal-metal, metal-oxide, and metal-mold were studied. For the first two interfaces, the experimental approach involved dipping a cold cylindrical metal into a liquid metal or liquid oxide, respectively. In this case, a shell freezes around the cylindrical addition and a thermal resistance develops during the existence of the shell. Data collected from a series of experiments were used as input into a model, which solves the inverse heat conduction problem in terms of a resistance estimate. Results for a variety of metal-metal and metal-oxide combinations indicated a relationship between the estimated and the mismatch of thermal expansion coefficients and thermal conductivities of interface materials. For the last interface metal-mold, the air gap size was measured and subsequently correlated with the interface thermal resistance. Various correlations will be presented, which predict the interfacial thermal resistance from the knowledge of the air gap at the metal-mold interface. Finally, some general guidelines will be presented on the values of thermal resistance at various interfaces.

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VISCOSITY MEASUREMENT OF ALUMINUM ALLOY CONTAINING SiC PARTICULATES: *Zhijing Zhang*[1]; Ramana G. Reddy[1]; Srinath Viswanathan[2]; [1]The University of Alabama, Dept. of Metall. and Mats. Eng., A129 Bevill Bldg., 126 Seventh Ave., P.O. Box 870202, Tuscaloosa, AL 35487-0202 USA; [2]Oak Ridge National Laboratory, Metals and Ceramics Division, Oak Ridge, TN 37831-6083 USA

The viscosity measurements were carried out on melts of 380 aluminum alloy containing 20 volume % SiC particulates under various shear rates at different temperatures using Brookfield viscometer. Results showed that viscosities of the melts increased with decreasing temperature and decreased with increasing shear rate. These results were compared with those of 356 alloy and it was found that the temperature had a more significant effect on viscosity of 356 alloy than that of 380 alloy containing SiC particulates. Based on the present experimental data an empirical viscosity model, which considers the effects of both solid fractions in the melt and shear rate, was proposed.

FUNDAMENTALS OF LEAD AND ZINC EXTRACTION AND RECYCLING: Pyroprocessing of Lead and Zinc—Primary Operations

Sponsored by: Extraction & Processing Division, Lead, Zinc, and Tin Committee

Program Organizers: A. Morris, San Diego, CA 92128 USA; Markus Reuter, Delft University of Technology, Netherlands

Wednesday PM Room: 7A
March 3, 1999 Location: Convention Center

Session Chairs: Arthur E. Morris, Thermart Software, San Diego, CA 92128-2720 USA; David G. Robertson, University of Missouri-Rolla, Dept. of Metallurgical Engineering, Rolla, MO 65409-1460 USA

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DEBISMUTHISING OF LEAD BY CENTRIFUGING: A. Arnold[1]; H. Sasker[2]; *Markus A. Reuter*[2]; J. Kruger[1]; [1]Aachen University of Technology, Institute for Nonferrous Process Metallurgy, Intzestrasse 3, Aachen Germany; [2]Technical University Delft, Raw Materials Processing, 120 Mijnbouwstraat, Delft 2628 RX The Netherlands

One method for removing bismuth during the refining of lead is the Kroll-Betterton process. In this final step of lead refining a calcium magnesium alloy is stirred into the lead creating compounds such as Bi2CaMg2, that can be skimmed off from the surface of the lead. This paper discusses methods to improve the recovery of bismuth and decrease the usage of magnesium and calcium as a "reagent" by presenting results on the following aspects: a fundamental thermodynamic study of the system to determine the conditions at which all possible compounds of Bi, Ca and Mg are created in the Pb - Bi - Mg - Ca system; for each of these compounds equilibrium constants and the theoretical stoichiometric quantity of Ca and Mg are determined; discuss the application of an experimental centrifuge to facilitate the bismuth refining; and apply the obtained fundamental information mentioned above to run tests in the above mentioned centrifuge to optimally recover bismuth from lead.

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FLASH ROASTING OF ZINC CONCENTRATES AND LEACH RESIDUES USING A TORBED REACTOR: *Chris E. Dodson*[1]; [1]Torftech (Canada) Inc., 2395 Speakman Drive, Mississauga, Ontario L5K 1B3 Canada

Conventionally hydrometallurgical zinc recovery processes from sulphide concentrates include roasting, leaching, precipitation, impurity removal and electrowinning. The use of the novel TORBED process reactor for the flash roasting of zinc sulphides will be proposed. The advantages in its application will be discussed including fine particle processing capability, lower cost smaller roasters, waste minimization, improved leaching efficiency and overall process simplification. Results from the ongoing pilot trials will be given.

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THE BEHAVIOUR OF GALLIUM DUIRNG JAROSITE PRECIPITATION: *J.E. Dutrizac*[1]; [1]CANMET, 555 Booth Street, Ottawa, K1A 0G1Canada

The behaviour and deportment of gallium during the precipitation of jarosite-type compounds from $Fe(SO_4)_{1.5}$ - M_2SO_4 (where M is Na, K or NH_4) solutions were investigated. Gallium is readily precipitated n all the jarosite-type compounds, and the extent of gallium precipitation increases as the Ga concentration of the solution increases. The Ga^{3+} ion replaces Fe^{3+} in the jarosite structure to form a nearly ideal solid solution series. The molar partitioning coefficient, $(Ga/Ga+Fe)_{solid}$ $(Ga/Ga+Fe)_{solutions}$ 1,0 for the three jarosite species studied. Increasing retention times significantly increase the amount of precipitate formed, but have only a minor effect on the composition of the jarosite products. Increasing concentrations of $Fe(SO_4)_{1.5}$, in the presence of a constant $Ga(SO_4)_{1.5}$ concentration, proportionally increase the amount of product, and result in a significant reduction of its Ga content. In contrast, increasing $ZnSO_4$ concentrations have a negligible effect on the amount of product formed or its Ga content. A comparison with previously published results for indium, shows that both Ga ad In behave very similarly during the precipitation of jarosite-type compounds.

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OPTIMISATION OF A TIN-LEAD-SMELTING FURNACE WITH THE AID OF DATA RECONCILIATION MODELLING TECHNIQUES: *S. C. Grund*[1]; *Markus A. Reuter*[2]; R. Janssen[2]; A. Nolte[3]; [1]Metallurgical Consultant, Alter Postweg 12, Dorsten 46282 Germany; [2]Technical University Delft, Raw Materials Processing, 120 Mijnbouwstraat, Delft 2628 RX The Netherlands; [3]Hüttenwerke Kayser AG, Kupferstrasse 23, Lunen D-44532 Germany

In secondary copper smelting as it is performed at Hüttenwerke Kayser in Lünen (Germany), zinc-, tin- and lead-containing flue dusts are produced as intermediate products. These flue dusts are further processed in a hearth furnace. Followed by certain refining operations a saleable tin-lead-alloy as well as a saleable zinc flue dust are produced. Even though the hearth furnace technology has been in use for this purpose for a long time, its performance is constantly challenged by the increasing complexity of the raw materials (Zn/Sn/Pb-flue dusts), and tightening economical and ecological boundaries. Therefore, continually optimum processing conditions have to be searched for in a system that is often fundamentally poorly definable. The use of data reconciliation for the calculation of accurate statistical sound mass balances is demonstrated for the tin-lead hearth furnace. These reliable mass balances are the basis for any further modelling of the process with the aim of robust furnace optimisation. Incorporating metallurgical knowledge and experience as well as different mathematical metallurgical modelling techniques, further studies are presented in which the recoveries of valuable and minor elements and their dependency on various process parameters are fundamentally examined. The aim of this modelling is: to optimise the recoveries of the valuable elements as a function of various process parameters (also poorly defined parameters such as feed characteristics, etc.); to minimise the energy consumption and the processing costs; and thus to keep the process competitive in a harsher economical and ecological surrounding. The modelling principles discussed here are transferable to other metallurgical operations and are especially suited for ill-defined pyrometallurgical processes.

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A DIRECT REDUCTION ZINC PROCESS: *Lamar S. Todd*[1]; David G. C. Robertson[2]; Hongjie Li[2]; [1]Process Development Associates, 107 N. Brier Rd., Amherst, NY 14228-3450 USA; [2]University of Missouri-Rolla, Metallurgical Engineering, 215 Fulton Hall, Rolla, MO 65409-1460 USA

The direct production of metal from a sphalerite concentrate is an attractive route for primary zinc. A series of operations and conditions have been selected to efficiently cause the following overall exothermic reaction: $ZnS + O_2 = > Zn + SO_2$. The process uses a continuous circulation of molten copper for material and energy transfer between the unit operations. Sulfide concentrate is reduced with an excess of superheated copper to make a copper alloy and white metal. The alloy is stripped of volatile metals under vacuum and some metals can be separately condensed. The residual copper and the white metal are fed into a copper converter to be blown with oxygen for desulfurizing and the superheated copper is recycled. The paper will include a detailed material flow sheet for the process, discussion of the operating conditions of the individual units, behavior of minor elements, and zinc quality.

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SOLAR THERMOCHEMICAL PRODUCTION OF ZINC: *A. Steinfeld*[1]; P. Haueter[1]; S. Miller[1]; R. Palumbo[1]; A. Weidenkaff[1]; [1]Paul Scherrer Institute, High-Temperature Solar Technology, Villigen PSI CH-5232 Switzerland

The solar thermal production of zinc is considered for the conversion of solar energy into storable and transportable chemical fuels. The ultimate objective is to develop a technically and economically viable technology that can produce solar zinc. The program strategy for achieving such goal involves research in two paths: a direct path via the solar thermal dissociation of ZnO, and an indirect path via the solar carbothermal and CH4-thermal reduction of ZnO. Both paths make use of concentrated solar radiation as the source for high-temperature process heat. The thermal dissociation requires elevated temperatures (above about 2000K) and the development of a novel solar process technology, while the carbothermal reduction requires more moderate temperatures (above about 1300K) and uses a combination of solar and conventional energy technologies. The use of natural gas as the reducing agent combines in a single process the reduction of ZnO and the reforming of CH4 for the co-production of zinc and synthesis gas. The chemical thermodynamics and kinetics for the reactions involved are briefly reviewed. A solar chemical reactor for reducing ZnO with natural gas is also described and recent experimental results of solar tests conducted at PSI solar furnace are presented.

GENERAL ABSTRACTS: Session 8 - Melting, Solidification & Microstructure Characterization

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

Wednesday PM Room: 12
March 3, 1999 Location: Convention Center

Session Chairs: John Silvestri, Allvac, Monroe, NC 28111-0539 USA; Anthony Mulligan,Advanced Ceramics Research, Tuscon, AZ USA

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MELTING OF PB NANOCRYSTALS: Kevin F. Peters[2]; *Jerome B. Cohen*[1]; Yip-Wah Chung[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]European Synchrotron Radiation Facility, Surface Science Group - ID3, B.P. 220, Grenoble, Cedex F-38043 France; [3]Northwestern University, Department of Materials Science and Engineering, 2225 North Campus Dr., MLSB, Room 2036, Evanston, IL 60208-3108 USA

The size-dependent melting and surface melting in ultra high vacuum has been demonstrated by x ray powder diffraction. Whereas some prior studies have measured the size-dependent melting temperature via the diffraction intensity, it is shown here that crystallite reorientation makes the diffraction intensity an unreliable indicator of melting. Instead the diffraction peak shape reveals the size-dependent melting via changes in the crystallite size distribution. Measurements showed that the melting temperature varies inversely with the crystallite size and quantitatively favors the liquid-skin melting model over the homogeneous melting model. Surface melting is demonstrated via the reversible growth of a

liquid skin just below the size-dependent melting temperature. This research was supported in part by the U. S. Department of Energy, Grant No. DE FG02 84ER45097.

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THE COOLING AND SOLIDIFICATION BEHAVIOR OF ALUMINUM AND ALUMINUM ALLOYS WELD: *Kimioku Asai*[1]; Eisaku Tokuchi[1]; [1]Musashi Institute of Technology, Dept of Mechanical Engineering, 1-28-1 Tamazutumi, Setagaya-ku, Tokyo 158 Japan

Weld solidification has always posed experimental difficulties. Experiments which had not ever been approached in this respect were successfully carried out in the TIG arc spot welding on a thin plate. In this first research, the actual temperature in welding thermal cycle was carefully measured with extremely small CA-thermocouples; a high speed camera was also set for direct observation of the crystal growth, by which operation the initial solidification point on the cooling curves were surely decided. The results were compared to Aluminum, 99.99% purity, and two significantly typical commercial Al-alloys, A2024 and A5083. Our results should be useful in consideration of any aspect of cooling behavior that effectively relate to an occurrence of the welding defects such as porosity or hot cracking. Mainly, the dynamic behaviour of solidification rate, cooling rate, and temperature gradient in weld metal are discussed.

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DEVELOPMENT OF A REFINED MICROSTRUCTURE BY DECOMPOSITION OF A METASTABLE PRECURSOR: *Katherine C. Chen*[1]; Fuming Chu[1]; Dan J. Thoma[1]; [1]Los Alamos National Laboratory, Materials Science and Technology, Mail Stop G770, Los Alamos, NM 87545 USA

Laves phase (AB_2) intermetallics hold great potential as high-temperature structural materials if their characteristic low-temperature brittleness can be circumvented. A two phase alloy (C15+bcc) in the Nb-Cr-Ti system has been shown to have promising mechanical properties. Development of this alloy has required specific alloy design methodologies, such as alloying and novel processing techniques. While conventional casting often produces large grains with the Laves phase along the grain boundaries, melt-spinning has been utilized to rapidly solidify the alloy into a metastable bcc phase. Upon consolidation (HIP) of these melt-spun ribbons, the metastable alloy decomposes into a desired microstructure with extremely fine phase distributions of the Laves phase. Mechanical properties are expected to improve significantly over the cast material. The microstructural control from this metastable processing route offers an approach to tailor the phase distributions necessary for optimized properties in Laves phase alloys. Characterization by optical microscopy, SEM, TEM, and XRD, as well as results from mechanical testing, will be presented.

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EFFECTS OF ELECTROMAGNETIC VIBRATIONS ON THE STRUCTURE OF Al-Si ALLOYS: *Alireza Radjai*[1]; Kenji Miwa[2]; [1]Japan Science and Technology Corporation, Materials Processing Dept., National Industrial Research Institute of Nagoya, 1-1 Hirate-cho, Kita-ku, Nagoya, Aichi 462 Japan; [2]National Industrial Research Institute of Nagoya, Materials Processing Dept., 1-1 Hirate-cho, Kita-ku, Nagoya, Aichi 462 Japan

Electromagnetic Vibrations induced in a conducting liquid by simultaneous application of alternating electric and stationary magnetic fields may lead into the formation and collapse of cavities, which can affect the solidification structure. In order to investigate this matter, hypo-eutectic and hyper-eutectic Al-Si alloys were subjected to strong electromagnetic vibrations under different cooling conditions in an experimental apparatus designed for this purpose. Profound effects were observed for both alloys. The mechanism of the effects was studied by inducing vibrations in a hyper-eutectic Al-Si alloy containing suspended silicon particles and interrupting the process at different temperatures before and after the start of solidification by water quenching. Photomicrographs clearly revealed that suspended silicon particles were crushed into small pieces by cavitation phenomenon both above and below the liquidus temperature. The crushed particles started to agglomerate just after the start of solidification and expelled to the outer boundaries of the sample as solidification proceeded.

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MICROSTRUCTURAL CHARACTERIZATION OF WASTE FORM INGOTS CAST FROM IRRADIATED MATERIALS: *Dennis D. Keiser*[1]; [1]Argonne National Laboratory, Nuclear Technology, P.O. Box 2528, Idaho Falls, ID 83403-2528 USA

A metallic waste form alloy that consists primarily of stainless steel (SS) and zirconium is being developed by Argonne National Laboratory to contain metallic waste constituents that are residual from an electrometallurgical treatment process for spent nuclear fuel. Actual ingots have been cast in an induction furnace in a hot cell using leftover cladding hulls from an electrorefiner. These ingots have been sampled using a core-drilling and an injection-casting technique. In turn, generated samples have been characterized using chemical analysis techniques and a scanning electron microscope equipped with energy-dispersive and wavelength-dispersive spectrometers. As-cast ingots contain the expected concentration levels of the various constituents, and the phases that develop are very similar to those for alloys generated using non-radioactive surrogates for the various fission products. One exception is the appearance of a small precipitate phase that contains the fission product tellurium.

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TEM CHARACTERIZATION OF THE EFFECT OF MIXED PROTON/NEUTRON FLUX ON MICROSTRUCTURAL EVOLUTION OF STRUCTURAL MATERIALS FOR ACCELERATOR PRODUCTION OF TRITIUM.: *Bulent Hakan Sencer*[1]; Gillian Mary Bond[1]; Frank A. Garner[2]; Stuart A. Maloy[3]; Walter F. Sommer[3]; M. James[3]; [1]New Mexico Tech, Materials and Metallurgical Engineering, Campus Station, Socorro, NM 87801 USA; [2]PNNL, Materials Resources Department, 902 Battelle Blvd., P.O. Box 999, Richland, WA 99352 USA; [3]Los Alamos National Laboratory, APT/TPO, MS H809, Los Alamos, NM USA

Materials in the target and blanket regions of spallation neutron sources (SNS) will be subjected to high fluxes of high-energy protons and neutrons. There are no available data on materials performance under the conditions that are be experienced by Production of Tritium (APT) target and blanket materials. As particle energy increases to above 200 MeV or so, a major new variable becomes important: copious transmutation products are generated and enter the material as impurities. High-energy proton/neutron irradiation is also expected to generate very high levels of helium and hydrogen; for example, high-energy protons produce about 100 times more helium than fourteen MeV neutrons. To investigate the effects of these conditions on the microstructure, TEM specimens of several alloys have been irradiated in the Los Alamos Spallation Radiation Effects Facility (LASREF) at the 800 MeV accelerator. The effects of this simulated APT irradiation on Al6061-T6, SS316L and Inconel 718 are being characterized to give a better understanding of the microstructural evolution and consequent mechanical properties.

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HIGH-RESOLUTION AEM STUDY OF PARAEQUILIBRIUM CEMENTITE PRECIPITATION IN ADVANCED ULTRA-HIGH STRENGTH STEELS: *Gautam Ghosh*[1]; Gregory Bruce Olson[1]; [1]Northwestern University, Materials Science and Eng., 2225 N. Campus Dr., Evanston, IL 60208-3108 USA

To support quantitative design and to understand secondary hardening behavior of advanced ultra-high strength steels, the precipitation of cementite prior to the precipitation of coherent M_2C phase is investigated using model alloys. The microstructure of cementite is investigated by transmission electron microscopy techniques. The concentration of substitutional alloying elements in cementite are quantified in high-resolution analytical electron microscopy using extraction replica specimens. Quantification of substitutional elements in cementite confirms its paraequilibrium state with ferrite at the very early stage of tempering. The thermodynamics and energetics of paraequilibrium cementite nucleation are analyzed using Thermo-Calc software, and the growth of paraequilibrium cementite is simulated using DICTRA software. These simulations provide further insight of the experimentally

observed microstructures. The implications of the results will be discussed in the context of alloy design.

GENERAL RECYCLING OF MATERIALS: Physical and Hydrometallurgical Processing

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 Metallic Materials, Berlin D-10623 Germany

Wednesday PM Room: 1A
March 3, 1999 Location: Convention Center

Session Chairs: Isrun Bohlinger, Technical University of Berlin, Institute of Metallic Materials, Berlin, D-10623 Germany; Andréa Moura Bernardes, Universidade Federal do Rio Grande do Sul, LACOR-DEMAT-UFRGS, Porto Alegre, Rio Grande do Sul (RS) 900035-190 RS Brazil; Courtney A. Young, Montana Tech, Dept. of Metallurgical Engineering, Butte, MT 59701 USA

2:00 PM OPENING REMARKS

2:05 PM
PROCESSING OF DRY CELL BY ORE PROCESSING METHODS: *Jorge Alberto Soares Tenório*[1]; Denise Corrêa de Oliveira[1]; Arthur Pinto Chaves[2]; [1]Escola Politécnica. University of São Paulo, Dept. of Metall. and Mats. Eng., Av. Prof. Mello Moraes, 2463, Cidade Universitária, São Paulo 05508-900 Brazil; [2]Escola Politécnica da USP, Mining Engineering, Av. Prof. Mello Moraes, 2373, Cidade Universitária, São Paulo 05508-900 Brazil

Household zinc based batteries contain some heavy metals such as zinc, manganese and mercury. There is a large effort from manufacturers in order to eliminate the last one. As a municipal waste, the disposal of batteries has become an increasing worry. The aim of the present work was to characterize dry batteries scraps, defining parameters and yields of each stage. This was done using unit processes of ore treatment. Such procedures have been chosen due to its low cost. The employed methods were hammer mill grinding, size classification, magnetic separation and flotation. The characterization step was done by chemical analysis and x-ray diffraction. After size classification, it was verified that 76.6% of the total amount of zinc was above 1.70mm. This fraction was constituted basically of zinc and some coarse pieces from the steel body, paper and plastics. This fraction was submitted to magnetic separation followed by aqueous flotation. The manganese concentration in the fractions above 6.35 mm was less tha n 2%. This means that there was low contamination by the paste in this fraction. This was due to the entrapment of the paste by scraps from the steel body and zinc cup during grinding.

2:30 PM INVITED PAPER
BEHAVIOR OF FERROMAGNETIC PARTICLES ON THE EDDY CURRENT ROTOR SEPARATING NON-FERROUS SCRAP METAL CONCENTRATE FROM AUTOSHRED: *Adam J. Gesing*[1]; Russel Jahnke[1]; Kevin Dehetre[1]; Richard Griser[1]; Dennis Reno[1]; Richard Wolanski[1]; [1]Huron Valley Steel Corporation, 41000 Huron River Dr., Belleville, MI 48111 USA

An eddy current separator, (ECR) is designed to separate non-magnetic (non-ferrous) electrically conducting (metallic) particles from non-conductive residue. An ECR consists of a rotor - a fast spinning roll surfaced with rows of permanent magnets of alternating polarity. The rotor is housed in a fiber-reinforced composite shell which acts as a conveyor headpulley. The non-ferrous metallic particles are repelled by the rotor out of the material stream passing over a conveyor headpulley effecting the desired metal/non-metal separation. The behavior of ferromagnetic particles - mainly iron and iron oxide - is quite different. These are strongly attracted to the magnets and small particles tend to align in the direction of the magnetic flux. Since the direction of the flux changes with the passage of each magnet pole the small particles spin at very high rates causing wear of the belt and the composite outer shell enclosing the rotor. Large particles can not spin but can be heated by the eddy current effects which can burn through the composite headpulley shell. We discuss practical implications of this behavior of iron and rust on the design, performance and maintenance of eddy current separators.

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WASTE PROCESSING OF MgO BAGHOUSE DUST USING PLASMA ARC TECHNOLOGY: *Steven Wayne White*[1]; Ramana G. Reddy[2]; [1]University of Alabama, Dept. of Chem.l Eng., P.O. Box 870203, Tuscaloosa, AL 35487 USA; [2]University of Alabama, Metallurgical & Materials Engineering, P.O. Box 870202, Tuscaloosa, AL 35487 USA

Plasma arc technology is increasingly being used to process a number of waste materials. In present research, plasma technology is being investigated to treat waste magnesium baghouse dust, which is a waste material from the Magnetherm process. This dust contains mostly MgO, but also contains Na_2O, CaO, and K_2O. Plasma energy is to be used along with a reducing agent to produce pure gaseous magnesium while keeping the other materials in a slag. The magnesium will then be collected by rapid quenching. A non-transferred arc plasma torch is ideal for this reaction because of its high enthalpy and improved energy efficiency over conventional methods. Thermodynamic calculations using the Gibb's Free Energy Minimization method are being employed to determine the most stable compositions of the materials at various temperatures. The reactor setup will eventually allow for treatment of other waste materials.

3:20 PM INVITED PAPER
CONTROL OF THE PROPERTIES OF ANODIC SLIMES IN COPPER ELECTROREFINING: *Gerardo Cifuentes*[1]; S. Hernández[1]; P. Navarro[1]; J. Simpson[1]; C. Reyes[1]; N. Cornejo[2]; [1]Universidad de Santiago de Chile, Departamento de Ingenieria Metalúrgica, Av. Lib. B.O'Higgins 3363, Santiago Chile; [2]Ventana-ENAMI, Superintendencia Refinería, Carretera F30 E Nordm; 58270, Puchuncaví, V Región Chile

This paper presents the relationship between the composition of the cathode and anodic slimes at copper electrorefining's Ventana-ENAMI Company. It is known that the purity of the cathode and the electrolytic treatment affect solids present in the bath. Anodic slimes properties (for example chemical and crystalline composition, sedimentation) were studied. The properties were modified by composition of the anode and current density. For the experiments anode material was doped with different amounts of lead. Appearance of Bindheimite ($Sb_2Pb_2O_7$ was confirmed. The specific gravity of this species is approximately 7.3 - 7.5 (25ºC/25ºC). At these values the most probability of sedimentation is given, at smaller values slimes decrease the sedimentability.

3:45 PM BREAK

4:00 PM INVITED PAPER
THE APPLICATION OF ELECTRODIALYSIS ON THE TREATMENT OF EFFLUENTS WITH HEXAVALENT CHROMIUM: Marco Antonio Siqueira Rodrigues[1]; *Andrea Moura Bernardes*[1]; Jane Zoppas Ferreira[1]; [1]Universidade Federal do Rio Grande do Sul, LACOR-DEMAT-UFRGS, Av. Osvaldo Aranha 99/706, Porto Alegre, Rio Grande do Sul (RS) 90035-190 Brazil

The possibilities for treating rinse waters from chromating bath by electrodialysis are discussed together with the possibilities of optimizing the treatment process for waste reduction and reuse of water and chemical products. An industrial effluent with 4600 ppm of Cr(VI), in addition to other metallic contamination, was used as work solution. This solution has been recirculated on an electrodialysis cell of three compartments, using exchange membranes Selenion AMT and CMT. A migration of dichromate ions into the anodic compartment was obtained, so that an extraction of circa 99.9% of Cr(VI) present on the solution was observed, resulting in water with a Cr(VI) concentration of 4 mg/l.

These results show that electrodialysis can be used to treat these effluents, and this water could be reused as rinse water. The solution of the anodic compartment, consisting at the beginning of the experiment of H_2SO_4, 0.1 N, reached 7200 mg/l of Cr(VI). This concentrate could be reused on the chromating bath, itself.

4:25 PM INVITED PAPER

ELECTROLYTIC OXIDATION OF CYANIDE ON PbO_2-COATED STAINLESS STEEL: *Gerardo Cifuentes*[1]; L. Cifuentes[2]; Roland Kammel[3]; J. Torrealba[1]; [1]Universidad de Santiago de Chile, Departamento de Ingenieria Metalúrgica, Av. Lib. B.O. Higgins 3363, Santiago Chile; [2]Universidad de Santiago de Chile, Departamento de Ingenieria de Minas, Tupper 2069, Santiago Chile; [3]Technische Universität Berlin, Institut für Metallische Werkstoffe, Metallhüttenkunde, Sekr. BH 15, Str. des 17. Juni 135, Berlin D-10623 Germany

Electrolytic oxidation offers an environmental safe way in order to remove cyanides from electroplating waste waters. In this paper process parameters are discussed. Lead(IV)-dioxide coatings have been produced on anodes made of stainless steel 316 and 316I. Precoating of the substrate with Ni allows the deposition of α-Lead(IV) dioxide (orthorhombic) and β-Lead(IV) dioxide (tetragonal), the β-modification being the most abundant. Catalytic surfaces were produced in order to accelerate the oxidation of cyanide. The electrochemical parameters were determined by experiment and simulation. The values obtained for the exchange current density (i_0), the charge transfer coefficient (α), and the limiting current density (i_L) are similar for both methods: i_0 -2 Am^2, α -0.87, and i_L -120 Am^{-2} for a 0.5 g/l solution of sodium cyanide.

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CONVERSION AND PURIFICATION OF COPPER ARSENATE PRODUCED FROM LIBERATION CELLS AT COPPER REFINERIES LTD, TOWNSVILLE, AUSTRALIA.: *Stuart Peter Johnston*[1]; [1]Mount Isa Mines, Ltd., Copper Refineries, Ltd., Technical Superintendent, Hunter St., Stuart, Townsville, Queensland 4811 Australia

Copper Refineries Ltd is the largest producer of refined copper cathode in Australia. Feed stocks include 100mtpa arsenic contained in anode material received from Mt Isa. The main recovery of arsenic material is achieved via the copper liberation section prior to nickel sulphate purification. Rather than stockpiling or dumping the impure copper arsenate material, the product is reprocessed, the copper recovered and the arsenic purified into a valuable arsenate byproduct. This product is sold as direct feed stock for the treatment of plantation timbers. The end result, arsenic entering the Copper Refineries flow sheet is managed to produce an environmentally safe, value added and marketable product.

5:15 PM CLOSING REMARKS

INTERCONNECTPACK; INTERCONNECTIONS FOR ELECTRONICS PACKAGING: Conductive Polymer

Sponsored by: Electronic, Magnetic & Photonic Materials Division,
Program Organizers: Gautam Ghosh, Northwestern University, Dept. of Mat. 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

Wednesday PM Room: 17A
March 3, 1999 Location: Convention Center

Session Chairs: E. Suhir, Lucent Technologies; R. A. Fournelle, Marquette University

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2:00 PM INVITED PAPER

Z-AXIS ANISOTROPIC ELECTRICALLY CONDUCTIVE POLYMER-MATRIX COMPOSITE MATERIALS WITH ONE NICKEL PARTICLE PER CONDUCTION PATH: Yunsheng Xu[1]; *Deborah D. L. Chung*[1]; [1]State University of New York at Buffalo, Dept. of Mech. & Aero. Engr., 608 Furnas Hall, Amherst, NY 14260 USA

Z-axis anisotropic electrically conductive polymer-matrix composite materials in adhesive or resilient stand-alone film (for separable interconnections) forms are useful for electronic packaging, as one film can replace an array of soldered joints. We have developed both forms by using nickle particles and a polymer matrix (epoxy for the adhesive form and polyvinylidene fluoride for the film form), such that there is one nickel particle per conduction path. The adhesive form was screen printable. The electrical, mechanical and microstructural characteristics of both forms are addressed.

2:30 PM INVITED PAPER

DEVELOPMENT OF CONDUCTING ADHESIVE MATERIALS FOR MICROELECTRONIC APPLICATIONS: *Sung K. Kang*[1]; S Purushothaman[1]; [1]IBM, T. J. Watson Research Center, P.O. Box 218, Rm. 37-250, Yorktown Heights, NY 10598 USA

Electrically and/or thermally conducting adhesive materials are classified into two categories depending on their conduction modes: isotropic and anisotropic materials. Silver-particle filled epoxy is the most common example of the class of isotropic materials which are conductive in all directions. This material has been long used in the electronic applications as a die-bonding material, where its good thermal conduction rather than its electrical conduction property is utilized. The silver-filled epoxy material has several limitations for high performance electrical interconnections, such as low electrical conductivity, increase in contact resistance during thermal exposure, low joint strength, corrosion issue due to silver migration, difficulty in rework, and so forth. The anisotropic conducting material provides electrical and/or thermal conduction only in one direction. An anisotropic conducting film (ACF) is used for interconnecting TAB mounted chips to a liquid crystal display panel, where fine pitch interconnection and low temperature assembly are required. In this paper, a brief review of the state-of-art conducting adhesive technology is provided. Subsequently, development of new conducting adhesive materials is presented for several different applications, which include high temperature materials for ceramic substrates, and lower temperature materials for organic substrates.

3:00 PM INVITED PAPER

UNDERSTANDING OF ANISOTROPIC CONDUCTIVE FILMS(ACFS)/ADHESIVES(ACAS) FOR PACKAGING APPLICATIONS: *Kyung W. Paik*[1]; Myung J Yim[1]; [1]Korea Advanced Institute of Science and Technology, Dept. of Mats. Sci. and Eng., 373-1 Yusung-Gu, Gusung-Dong, Taejon, Chung-Nam Korea

Anisotropic conductive films (ACFs) or adhesives (ACAs) composed of an adhesives polymer resin and fine conductive fillers such as metallic particles or metal-coated polymer balls are key materials for fine pitch chip-on-film (COF) and chip-on-glass (COG) LCD packaging and also flip chip on organic board technologies. To understand the efficiency of electrical conduction in ACFs/ACAs, the theoretical electrical conduction model with physical contact mechanism has been simulated and experimentally proved. Three pressure dependent models - 1) elastic deformation Hertz contact model, 2) plastic deformation model and 3) FEM model, were developed. It was shown that the electrical contact resistance of ACF depends on numerous variables such as applied bonding pressure, bonding temperature/time (resin curing characteristics), number, size, mechanical and electrical properties of conducting particles. Electrical conduction through the pressure engaged contact area between conductive particles and conducting substrate pads is the major conduction mechanism in ACFs/ACAs interconnection. The effects of these variables on the conduction will be presented. Environmental effects on contact resistance and adhesion strength of ACFs/ACAs such as thermal aging, high temperature/humidity aging, and temperature cycling were investigated. And for the reparability of ACFs/ACAs interconnect, the adhesion property at various temperatures will be also presented. Finally, as one of the flip chip interconnect alternatives,

issues of using ACFs/ACAs materials for flip chip on organic substrates will be discussed.

3:30 PM BREAK

3:40 PM INVITED PAPER

BARE CHIP INTERCONNECTION USING AN ANISOTROPIC CONDUCTIVE ADHESIVE: *T. Sato*[1]; H. Date[1]; H. Tokuhira[1]; M. Sasaki[1]; E. Horikoshi[1]; M. Kawarada[1]; [1]Fujitsu Laboratories, Ltd., 10-1 Morinosato-Wakamiya, Atsugi 243-0197 Japan

A new anisotropic conductive adhesive, which might be a promising candidate for less 100 μm fine pitch flip-chip face down interconnect, has been developed. This material contains a filler which consists of a silver particle coated with a thin dielectric resin and an epoxy base adhesive. The conductive adhesive shows a very low interconnecting resistance of several milliohms, and a maximum permissible current of 4000 mA. Moreover, when LSIs are mounted on a circuit board, the adhesive shows a high electrical resistance even after a 500 h high-temperature high-humidity bias test (85°C, 85% R.H., and DC 5V). The change in electrical resistance was found to be less than 10% after thermal cycles test of 1000 cycles in the temperature range of -55°C to +125°C. These reliability characteristics would be sufficient for use in most of the microelectronic devices. An example of practical application in a hard disk drive circuit board will be given in this paper. Also, the effects of parameters such as adhesive strength, adhesive layer thickness, deformation behavior of the electrode on the substrate, and quality and quantity of the metal filler on the reliability charateristics will be discussed.

4:10 PM INVITED PAPER

TRANSIENT LIQUID PHASE SINTERING CONDUCTIVE ADHESIVES: POLYMER ADHESIVES WITH METALLURGICAL BONDS: *Catherine Shearer*[1]; Bryan Shearer[1]; Goran Matijasevic[1]; [1]Ormet Corporation, 2236 Rutherford Rd., #109, Carlsbad, CA 92008 USA

Conductive adhesives which have a metallurgically alloyed web with an interpenetrating polymer have been developed to mitigate some of the deficiencies of standard particle-filled conductive adhesives. The metal network is formed in situ by a process known as transient liquid phase sintering (TLPS) and is mutually reinforcing with the polymer network. Bulk as well as interface electrical connections are metallurgically alloyed providing stable electrical and thermal conduction. These new conductive adhesive compositions are compatible with bare copper as well as alloy surface finishes. The TLPS conductive adhesives utilize conventional solder paste dispensing and processing equipment. Electrical conductivity results indicate that the values are close to those of solder alloys. This type of adhesive has been tested for surface mount component attach, in which boards were subjected to drop tests and environmental exposure. All components, including J-lead type, survived this test, as would be expected of typical solder joints. Reliability testing including humidity exposure and thermal cycling has demonstrated that this type of adhesive performs substantially better than standard, passive filler loaded conductive adhesives.

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FRACTURE BEHAVIORS OF LEADFRAME/EPOXY INTERFACE UNDER VARIOUS LOADING CONDITIONS: *H. Y. Lee*[1]; Jin Yu; [1]Korea Advanced Institute of Science and Technology, Dept. of Mats. Sci. and Eng., Taejon 305-701 Korea

Popcorn cracking of thin plastic packages is a serious problem in the microelectronics packaging industry, and ways to improve inherently poor adhesion between leadframe and epoxy is an important issue. Here, copper based leadframes were oxidized in two kinds of hot alkaline solutions, brown and black oxide forming, and molded with epoxy molding compound. Then, the adhesion strengths of the leadframe/epoxy interfaces were measured by using sandwiched double cantilever beam (SDCB), pull-out, and sandwiched Brazil-nut (SBN) specimens. Loading conditions of the SDCB and pull-out specimens were close to the mode I and mode II, respectively, and in-between mode I and mode II for the SBN specimens. After the adhesion measurements, fracture surfaces were analyzed by SEM, XRD and EDX. Results indicates that adhesion strength, in terms of critical energy release rate(Gc)or the pull strength, is directly relate to the formation of acicular CuO precipitates at the interface. However, once a continuous layer of CuO precipitates formed either on the leadframe or underlying Cu2O layer, interface toughness saturated regardless of further oxide thickening. For SBN specimens, Gc increased with phase angle, but kinking of interface cracks into epoxy were observed in a systematic manner. For all cases, size of the acicular precipitates was found to have secondary effects on the toughness.

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INTERFACIAL FRACTURE ENERGY MEASUREMENTS IN THE Cu/Cr/POLYMIDE SYSTEM: *Y. B. Park*[1]; I. S. Park[1]; Jin Yu[1]; [1]Korea Advanced Institute of Sciece, Dept. of Mats. Sci. and Eng., Taejon 305-701 Korea

The interfacial fracture energies(%C) of the Cu/Cr/polyimide system were deduced under varying Cu film thickness and pretreatment conditions based on two methods X-ray measurement by Park and Yu[1] and theoretical methods by Moidu et al.[2]. The two methods showed reasonable agreement for most cases, imparting validity for both approaches. Estimated %C were quite independent of the metal film thickness and increased with the rf plasma power density of polyimide pretreatment as expected. Estimated %C values were 46.8 - 17.8, 170.3 - 42.9 and 253.9 - 44.4 J/m^2 for the rf plasma power density of 0.03, 0.036 and 0.05W/cm2 respectively. To the author's knowledge, this work is the first in the actual estimation of the interfacial energy in the Cu/Cr/polyimide system. Then, well known fracture mechanics solutions for two layer (substrate/thin film) structure were extended to cover the three layer(substrate/interlayer /thin film) structure using the path independence of the J integral. Application of the result to the peel test of Cu/polyimide/alumina system using FEM showed that the phase angle was nearly constant with the film thickness , but using the two layer solution led to a substantially large underestimation of the phase angle. [1] I.S.Park and Jin Yu: Acta Mater. 46, 2947 (1998) [2] A.K.Moidu, A.N.Sinclaire and J.K Spelt: J. Testing Eval. 26,247(1998)

INTERNATIONAL SYMPOSIUM ON ADVANCES IN TWINNING: Transformation Twinning and Mechanisms

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 Laboratory, Mats. Sci. & Tech. Div., Washington, D.C. 20375-5000 USA

Wednesday PM Room: 17B
March 3, 1999 Location: Convention Center

Session Chairs: Manfred Wuttig, University of Maryland, Dept. of Mats. & Nuclear Eng., College Park, MD 20742-2115 USA; K. T. Ramesh, The Johns Hopkins University, Dept. of Mech. Eng., Baltimore, MD 21218-4316 USA

2:00 PM INVITED PAPER

NANO-AND MESO-TWINNING IN TRANSFORMING ALLOYS: Harsh Deep Chopra[1]; *Manfred Wuttig*[1]; [1]University of Maryland, Materials and Nuclear Engineering, Bldg. 090, Rm. 2135, Stadium Drive, College Park, MD 20742-2115 USA; [1]SUNY at Buffalo, Mech. & Aerospace Eng. Dept. & Center for Advanced Photonic & Electronic Materials, Materials Progam, Room 613, Furnas Hall, Buffalo, NY 14260-4400 USA

This paper covers nano-twinning in In-Tl, In-Cd and Fe-Pd alloys of average fcc high temperature (austenitic) and meso-twinning in In-Tl of fct low temperature (martensitic) symmetry. In the former nano- twinning manifests itself through the low frequency "elastic" shear anisot-

ropy, 2C44/(C11-C12), which approaches a value of one as the temperature is lowered towards the martensitic transformation temperature. Bending experiments of martensitic In-Tl polydomain single crystals in the ferroelastic and rubberlike temperature regimes, accompanied by in situ video recordings of the evolving mesostructure, revealed that the deformation is controlled by the rotation of twin boundaries. The experimental ratios of the twin and elastic modules demonstrate that twins of the second hierarchy control the deform.

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THE SHAPE MEMORY EFFECT IN RUTHENIUM ALLOYS: *Richard W. Fonda*[1]; [1]The Naval Research Laboratory, Physical Metallurgy Branch, Code 6324, Washington, D.C. 20375 USA

Near-equiatomic alloys of niobium-ruthenium and tantalum-ruthenium have recently been shown to exhibit a shape memory behavior at elevated temperatures. These alloys have a B2-ordered cubic structure at high temperatures which transforms during cooling to a highly twinned tetragonal microstructure. Some compositions undergo an additional transformation to a monoclinic structure. The cubic-to-tetragonal transformation, which is responsible for the shape memory effect in these alloys, varies with composition from near room temperature to near 1000ϒC for Nb-Ru and to well over 1000ϒC for Ta-Ru. These are among the highest temperature shape memory transitions yet discovered. This talk will describe the shape memory effect in these alloys and how it relates to the observed transformations and microstructures.

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TWIN INTERSECTIONS WITH GRAIN BOUNDARIES: *Alexander H. King*[1]; [1]State University of New York, Dept. of Mats. Sci. and Eng., Nicolls Rd., Stony Brook, NY 11794-2275 USA

We consider the thermodynamic stability of the junctions between twins and grain boundaries in a formalism that includes anisotropic interfacial energies. General relationships between the interfacial energies and the dihedral angles at twin-grain boundary intersections are derived and we show that there exists a number of special cases. Although the dihedral angles opposite twins are frequently observed to be close to 180 degrees, this angle can only be achieved under very special circumstances: we show that these are not, however, restricted to the case of negligible twin boundary energy. We derive general rules and relationships that allow for grain boundary energy to be measured by using the twin boundary as a "probe" of known energy. Acknowledgment: this work is supported by the NSF, grant number DMR9530314.

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POLYTWIN HETEROSTRUCTURES: *Alexander L. Roytburd*[1]; [1]University of Maryland, Mats. and Nuclear Eng., Bldg. 090, Rm. 1104, College Park, MD 20742 USA

The polytwin heterostructures can be formed as a result of phase transformation or deformation in constrained layers, composed of epitaxial couples or multilayers. Due to the elastic interaction between the layers of a heterostructure, these layers transform into sets of periodically alternating lamellae, or elastic domains. A polydomain layer can consist of either differently oriented domains of the same phase (twins) or domains of different phases. The former case is considered here. The goal of this paper is to determine the parameters of the polytwin heterostructures and the conditions for their formation, i.e., their dependence on the characteristics of phase transformations, lattice misfits and the film thickness, as well as external stress. If the interdomain interfaces are mobile, their movement under external stresses results in superelastic deformation. The giant increase of compliance and susceptibility should be expected at the critical thicknesses of the polytwin layer. These critical thicknesses correspond to loss of stability of the polytwin structure or change of polytwin symmetry. This work was supported by Office of Naval Research under Grant No.: N00014-93-10506 and National Science Foundation under the Grant No.: DMR-9633638.

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COMPETING EFFECTS OF SLIP AND TWINNING ON THE FLOW STRESS OF HADFIELD MANGANESE STEEL SINGLE CRYSTALS: Ibrahim Karaman[1]; Ken Gall[1]; *Huseyin Sehitoglu*[1]; Yuriy I. Chumlyakov[2]; [1]University of Illinois, Mech. & Indust. Eng., 1206 W. Green St., Urbana, IL 61801 USA; [2]Siberian Physical-Technical Institute, Revolution Sq. 1, Tomsk 61801 Russia

A systematic study on Hadfield Manganese steel single crystals (Fe-13wt.%Mn-1.0wt.%C) has been performed to better understand the work hardening mechanisms in polycrystalline Hadfield Steel. The artificially grown single crystals are free of grain boundary interactions, and hence facilitate useful discussions on the deformation mechanisms of fcc alloys with a low stacking fault energy (SFE) and high interstitial content. The main objective of this single crystal study is to examine the dependence of the monotonic tensile and compressive stress-strain behavior on crystal orientation, loading direction, and test temperature. A strong orientation dependence of the governing deformation mechanism, strain hardening coefficient, and extent of different strain stages were detected along the [111], [001], [321] directions. To determine the governing deformation mechanism, the deformed samples were studied with both metallurgical and diffraction techniques. It is shown that twinning is primary deformation mechanism in [111] crystals under tension and in [001] crystals under compression at all test temperatures ranging from 113K to 293K. In the aforementioned crystals, twinning is observed as a softening mechanism and an extended Stage I deformation regime is realized, which is not common for these orientations. During stage II deformation, primary twin-secondary twin and slip-twin interactions play an important role in the strain hardening of these single crystals. In [321] crystals deformed at 293K, after an extended stage I hardening, primary slip-primary twin interactions cause an anomalous stage II hardening. Conversely, the lower stage II hardening coefficient of these crystals at 113K is attributed to the difficulty of cross-slip and easiness of twinning at low temperatures. From these single crystal results, it can be summarized that the competing effects of slip and twinning and the interaction of the two deformation mechanisms make substantial contributions to the work hardening. The increased friction force due to high content of interstitial carbon is proposed to have a contribution to the observed dependence of deformation mechanism along different orientations. The passage of the leading partial dislocation in a low stacking fault energy fcc material transforms the position of the interstitial atom from an octahedral to a tetrahedral site. This transition causes orthorombic distortion providing an extra friction force on the trailing partials, and further increasing the work hardening of this material.

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TWIN COMPONENTS IN RECRYSTALLIZATION TEXTURES OF ROLLED Fe-Ni ALLOYS AND SILVER ELECTRODEPOSITS: Hyo-Tae Jeong[1]; Hyo-Seung NAM[1]; *Dong Nyung Lee*[2]; [1]Seoul National University, Research Center for Thin Film Fabrication and Crystal Growing of Advanced Materials, San 56-1, Shinrimdong, Seoul, Kwanakgu 151-742 Korea; [2]Seoul National University, Materials Science and Engineering, San 56-1, Shinrimdong, Seoul, Kwanakgu 151-742 Korea

The evolution of recrystallization textures from plastically deformed and electrodeposited metals has been relatively well explained based on the energy release maximization theory(ERMT) advanced by one of the present authors(LEE). In the model, the absolute maximum normal stress direction of a deformed or fabricated material becomes parallel to the direction of the minimum elastic modulus of recrystallized grains, whereby the energy release during recrystallization can be maximized. However, the recrystallization textures of cold rolled Fe - 36 to 51% Ni alloys and silver electrodeposits, which have low stacking fault energies, were found to have major orientation components predicted by ERMT and their twin components. The relative intensity of twin component in the recrystallization of the Fe-Ni alloys decreased with increasing Ni content due to the increase in stacking fault energy. Therefore, the twin component cannot be avoided in the recrystallization textures of low stacking fault energy materials.

INTERNATIONAL SYMPOSIUM ON GAMMA TITANIUM ALUMINIDES: TiAl Alloys: New Alloys and Oxidation

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

Wednesday PM Room: 8
March 3, 1999 Location: Convention Center

Session Chairs: Hubert I. Aaronson, Department of Materials Science & Engineering, Carnegie Mellon University, Pittsburgh, PA 15213 USA; Shigeji Taniguchi, Osaka University, Dept. of Mats. Sci. and Proc., Suita, Osaka 565 Japan

2:00 PM INVITED PAPER
DEFORMATION AND FRACTURE OF BI-PST AND TRI-PST CRYSTALS AND DS INGOTS OF TiAl-BASE ALLOYS: Dai Imamura[1]; Hiroaki Hoshikawa[1]; Kyousuke Kishida[1]; Haruyuki Inui[1]; *Masahara Yamaguchi*[1] [1]Kyoto University, Dept. of Mat. Sci. & Eng., Yoshida Honmachi, Sakyo-ku, Kyoto 606-8501 Japan

We have currently been working to develop directional solidification (DS) techniques to grow ingots of TiAl-base alloys composed of many columnar grains with the lamellar structure aligned along the growth direction. One of the major factors controlling the mechanical properties of such DS ingots is expected to be compatibility requirements imposed at grain boundaries of columnar grains since each columnar grain, which is a PST crystal, deforms in quite an anisotropic manner. Thus, to understand the mechanical properties of DS ingots, the conditions governing the compatibility of deformation for two adjacent columnar grains and their interaction in terms of both microscopic and macroscopic effects are required. For this purpose, we have been carrying out a systematic experimental study on the deformation and fracture of bi-PST and tri-PST crystals. Recent results of the study are summarized and their implications for the deformation of DS ingots are then discussed.

2:30 PM INVITED PAPER
MICROSTRUCTURE AND PROPERTIES OF HIGH-Nb CONTAINED TiAl-BASED ALLOYS: *Guoliang Chen*[1]; W J. Zhang[1]; Z. C. Liu[1]; S. J. Li[1]; *Young-Won Kim*[2]; [1]Univeristy of Science & Technology, State Key Laboratory for Advanced Metals & Materials, Beijing 100083 PR China; [2]UES, 4401 Dayton-Xenia Road, Dayton, OH 45432 USA

This paper summarizes our recent studies in the phase relationships, microstructure evolution/control, and tensile and creep properties in the Ti-(44~47)Al-(8~10Nb) alloys. The following aspects have been experimentally observed: 1) The Nb additions decrease the Ta and stabilize the B2 phase; 2) The a field is narrowed down by these additions; 3) A ternary g+a+B2 phase field was confirmed at 1050~1250℃; 4). The stacking fault energy in the g-TiAl phase is reduced, thereby promoting twinning and improving high temperature creep resistance; 5) Activation of both ordinary and super-dislocations was observed in Ti-45Al-10Nb deformed at RT as well as 900℃. The CRSS for ordinary dislocation slip in the g phase is increased; 6) The presence of B2 phase appears to be detrimental to the RT ductility and high temperature strength; 7) Various types of substructures formed by hot deformation may influence the microstructural stability at high temperature. From these results, key points for the future development of high-Nb containing gamma TiAl alloys are discussed.

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TiAl-BASED INTERMETALLICS: THE PHASE EQUILIBRIA GAMMA TiAl-ALPHA2 Ti3Al-PSI IN THE SYSTEMS WITH V,Cr,Mn,Fe,Co,Ni,Nb,Mo,Ru,Rh,Pd,Ta,W,Re,Os,Ir AND Pt: *Peter Franz Rogl*[1]; Jin Jun Ding[1]; Helmut Schweiger[1]; *Raimund Podloucky*[1]; [1]Universität Wien, Institut für Physikalische Chemie, Währingerstrasse 42, Wien A-1090 Austria

Strengthening of gamma-TiAl based intermetallics via solution and/or precipitation hardening involving third metal components, essentially depends on a detailed knowledge of the temperature and solute dependent solubility limits as well as of the chemical and crystallographic nature of the precipitate. We present the phase relations in a series of partial ternary systems Ti-Al-M particularly in the region bound by the phases gammaTiAl-alpha2Ti3Al-psi where M=V,Cr,Mn,Fe,Co,Ni,Nb,Mo,Ru,Rh,Pd,Ta,W,Re,Os,Ir,Pt and psi is the ternary compound in equilibrium with gamma and alpha2. The investigations are based on quantitative X-ray powder diffraction, light optical microscopy and EPMA. Solubility limits at 950℃ are derived for M in both gamma-TiAl and alpha2-Ti3Al. The phases psi and their crystal structures have been identified. Results of first principles calculations studying the site occupation of ternary additions of 3d, 4d, 5d elements are presented.

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THE OXIDATION BEHAVIOUR OF HIGH STRENGTH TiAl ALLOYS UNDER ISOTHERMAL AND CYCLIC EXPOSURE: *Alan Partridge*[1]; [1]DERA, Structural Materials Centre, Ively Rd., Farnborough, Hants GU14 0LX UK

Currently the maximum operating temperature of g-TiAl based alloys for aero-engine applications is limited to around 750℃; as a consequence of the rapid deterioration in oxidation resistance at higher temperatures. Recently a series of alloys have been developed, which contain up to 8 at.% (Nb, Hf, Zr, Ta) alloying additions. The oxidation behaviour of these alloys has been evaluated under both isothermal and cyclic oxidation conditions, and have been observed to display much improved oxidation resistance compared to traditional g-TiAl alloys with lower alloying additions. Detailed analyses of the oxidised samples have been performed; including high resolution EBSD analysis of the phases at the scale-metal interfaces. The results of these studies will be presented and mechanisms to explain the improved oxidation resistance will be proposed.

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A COMPARATIVE STUDY OF OXIDATION RESISTANCE OF ENGINEERING GAMMA TiAl ALLOYS: *Michiko Yoshihara*[1]; Young-Won Kim[2]; [1]Yokohama National University, Mech. Eng. and Mats. Sci., 79-5, Tokiwadai, Hodogaya-ku, Yokohama, Kanagawa 240-8501 Japan; [2]UES, Inc., Materials and Processes Division, 4401 Dayton-Xenia Road, Dayton, OH 45432-1894 USA

Gamma TiAl alloys have attractive properties for high temperature structural applications, with their use temperature limited by the oxidation and/or creep resistance. For the last ten years, various engineering gamma alloys have been developed in an effort to enhance the performance levels, often without the oxidation-resistance given a serious consideration. In this study, systematic experiments have been conducted to quantify and compare the oxidation behavior of typical engineering gamma alloys. The selected alloys include: Cast 4822 (Ti-47Al-2Cr-2Nb), cast 45XD (Ti-45Al-2Mn-2Nb-0.8TiB_2), cast 47XD (Ti-47Al-2Mn-2Nb-0.8TiB_2), wrought 395 (Ti-46.5Al-2Cr-2Nb-1Mo-0.2B), wrought K5S (Ti-46.2Al-2Cr-3Nb-0.2W-0.1Si), wrought KDCBS (Ti-46.4Al-2Cr-3Nb-0.2W-0.1B-0.2C-0.1Si), wrought 96F (Ti-46.5Al-2Cr-2.8Nb-0.2W-1Hf), wrought 95G (Ti-45Al-10Nb) and wrought 97G (Ti-45Al-8Nb). The oxidation tests were performed in air, with the isothermal exposures up to 200h and 2h-cyclic exposures up to 1000h at 760℃ and 870℃. Two Ti-Al binaries (Ti-46Al and Ti-50Al) and a conventional superalloy (Inconel 713C) were also tested as references. Detailed results will be discussed.

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ISOTHERMAL AND CYCLIC OXIDATION BEHAVIOR OF TITANIUM ALUMINIDES: *Lorenz Singheiser*[1]; Willem J. Quadakkers[1]; [1]Forschungszentrum Juelich GmbH, Institut für Werkstoffe und Verfahren

der Energietechnik 2, Leo-Brandt-Str., Juelich, NRW D-52425 Germany

The paper reviews the oxidation behavior of different titanium aluminides under isothermal and cyclic oxidation conditions in the temperature range from 700ϒC to 900ϒC. Special attention will be given on the role of different alloying elements as well as on the influence of gas phase composition on the oxidation kinetics and oxide composition. The effect of niobium in terms of its influence on the aluminum and titanium activity as well as on the microstructure of the subscale composition will be discussed. Niobium has a significant influence on the solubility of oxygen as well as nitrogen and seems to stabilize a so-called x-phase, which corresponds to an Al-rich oxygen containing Ti3Al. As long as this subscale phase is uniform alumina will be formed. Results will be presented how the stability of this phase can be increased by further alloying elements resulting in significant improved oxidation resistance of modified titanium aluminides compared with niobium containing alloys. The current status of coating development for titanium aluminides will be reviewed as well and the different approaches to improve oxidation and hot corrosion resistance will be discussed.

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INFLUENCE OF WATER VAPOR ON THE MECHANICAL PROPERTIES OF TiAl AT HIGH TEMPERATURES: *Andreas Zeller*[1]; Franz Dettenwanger[1]; *Michael Schütze*[1]; [1]DECHEMA e.V., Karl-Winnacker-Institut, Theodor-Heuss-Allee 25, Frankfurt am Main, Hessen D-60486 Germany

Recently, more attention is given to the influence of water vapor on the oxidation behaviour and the mechanical properties of TiAl, since it is known that water vapor embrittles intermetallic compounds, leading to a deterioration of the mechanical properties. At high temperatures a competition between surface oxidation and hydrogen attack seems to occur for TiAl. In order to evaluate the influence of water vapor on the oxidation and mechanical behaviour of TiAl based alloys, thermogravimetric analysis, creep and LCF-tests were conducted at 700ϒC in dry air and air containing a defined content of water vapor. In creep tests, the presence of water vapor leads to an increase in the primary creep strain, but the following minimum strain rate in the secondary creep regime does not show any significant difference. Therefore the cracking frequency of the protective oxide scale during deformation seems to play the key role for the extent of hydrogen attack on TiAl at 700ϒC. In LCF-tests the negative influence of water vapor is more pronounced, since the oxide scale is continuously damaged and the attack can proceed throughout the whole test. The paper will report and discuss the results of the mechanical tests, with focus on the influence of water vapor on oxide scale formation, on the Al-depleted subsurface layer as well as on crack initiation and propagation processes.

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THE INFLUENCE OF HIGH TEMPERATURE OXIDATION ON THE PERFORMANCE OF TWO GAMMA TiAl-BASED ALLOYS: *Marinus Frederik Stroosnijder*[1]; Jan Sunderkoetter[1]; Helmut Clemens[2]; Hans Peter Martinz[3]; Wolf Knabl[3]; [1]European Commission, Institute for Advanced Materials, Via Fermi 1, Ispra 21020 Italy; [2]Universitaet Stuttgart, Institut fuer Metallkunde, Seestrasse 71, Stuttgart 70174 Germany; [3]Plansee AG, Technology Center, Reutte, Tirol 6600 Austria

The isothermal and cyclic oxidation behaviour of two gamma TiAl-based alloys, i.e. Ti-47Al-2Cr-0.2Si and Ti-48Al-2Cr-2Nb (at%), was studied at 800ϒC in air. Ti-48Al-2Cr-2Nb showed the lowest oxidation rate and the highest spallation resistance. For Ti-47Al-2Cr-0.2Si a low isothermal oxidation rate but pronounced susceptibility for oxide spallation was found. During oxidation a complex multi-phased and -layered scale was formed on the surface of the alloys. In order to study the influence of oxidation on mechanical properties, 4-point bending tests were conducted at room temperature and 800ϒC on specimens which were pre-oxidized in air for different exposure times at 800ϒC. Although rather massive oxide scales had formed, no negative effect on the bending properties (strength, bending angle) at high temperature was observed. At room temperature, however, a significant degradation occurred. This behaviour can be attributed to brittle phases at the interface, which act as crack initiation sites below the brittle-to-ductile transition temperature.

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AN INVESTIGATION OF FRACTURE AND FATIGUE CRACK GROWTH IN CAST LAMELLAR Ti-48Al- 2Cr-2Nb: C. Mercer[1]; L. Jun[1]; F. Ye[1]; W. O. Soboyejo[1]; [1]Department of Materials Science and Engineering, The Ohio State University, 2041 College Road, Columbus, OH 43210-1179

The results of a recent study of fracture toughness and fatigue crack growth in cast lamellar Ti-48Al-2Cr-2Nb will be presented in this paper. These include: the effects of loading rate on fracture initiation toughness and resistance- curve behavior, and the effects of temperature on fatigue crack growth. Loading rates corresponding to stress intensity factor increase rates between 1 and 100 MPa ”m per second will be shown to have only a limited effect on the fracture initiation toughness (approx. 20 MPa ”m) and resistance-curve behavior at room-temperature. However, temperature is shown to have a significant effect on the fatigue thresholds and growth rates between 25 and 700 C. The trends in the fatigue crack growth rates and thresholds are rationalized by considering the combined effects of crack-tip deformation and oxide-induced crack closure. The observed crack-tip shielding mechanisms are also modeled using micromechanics concepts.

LONG TERM STABILITY OF HIGH TEMPERATURE MATERIALS: Stability of Ni-base Alloys - II

Sponsored by: Structural Materials Division, High Temperature Alloys Committee, Physical Metallurgy Committee
Program Organizers: Gerhard E. Fuchs, Lockheed Martin Corporation, Schenectady, NY 12301-1072 USA; Kathryn A. Dannemann, Southwest Research Institute, San Antonio, TX 7828-0510 USA; Todd C. Deragon, Special Metals Corporation, New Hartford, NY 13413-5392 USA

Wednesday PM Room: 9
March 3, 1999 Location: Convention Center

Session Chair: Kathryn A. Dannemann, Southwest Research Institute, San Antonio, TX 7828-0510 USA

2:00 PM INVITED PAPER

INVESTIGATION OF THE FORMATION OF TOPOLOGICALLY CLOSE PACKED PHASE INSTABILITIES IN NICKEL-BASE SUPERALLOY RENE N6: *Frank J. Ritzert*[1]; David R. Arenas[2]; Vijay K. Vasudevan[3]; [1]NASA Lewis Research Center, Materials Division, 21000 Brookpark Rd., MS 49-1, Cleveland, OH 44135 USA; [2]The Pennsylvania State University, Dept. of Mats. Sci. and Eng., 209 Steidle Bldg., University Park, PA 16802 USA; [3]University of Cincinnati, Dept. of Mats. Sci. and Eng., 497 Rhodes Hall, ML #12, Cincinnati, OH 45221 USA

Topologically close packed (TCP) phase instability in third generation Ni-base superalloys is understood to hinder component performance when applied in high-temperature jet engine applications. The detrimental effects on high temperature performance from these brittle phases includes weakening of the Ni-rich matrix through the depletion of potent solid solution strengthening elements. Thirty-four compositional variations of polycrystalline Rene N6 were defined from a design-of-experiments approach and then cast, homogenized, and finally aged to promote TCP formation. Our prior work reported on the results of the multiple regression modeling of these alloys in order to predict the volume fraction of TCP. This paper will present further results on these alloys including elemental partitioning, kinetics, and comparison to other models.

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FORMATION OF ALPHA-Cr IN ALLOY 718 WITH VARYING Cr AND Nb LEVELS DURING LONG TERM AGING: *B. A. Lindsley*[1]; G. E. Maurer[1]; J. F. Radavich[2]; [1]Special Metals Corporation, 4317 Middle Settlement Rd., New Hartford, NY 13413 USA; [2]Micromet, West Lafayette, IN USA

Alloy 718 is commonly used in gas turbine disks at operating temperatures up to 649°C. Above this critical temperature, the γ" strengthening phase rapidly transforms in to delta phase and γ', resulting in a loss of tensile and impact properties. Below this temperature, the γ" is relatively stable, however, impact properties were found to drop off significantly after exposures below 649°C. Early work by Radavich found that α-Cr precipitated in retired Alloy 718 turbine disks after 28,000 hours of service. The α-Cr formed primarily along grain boundaries in association with delta phase at operating temperature of 593°C up to 718°C and was responsible for the drop in impact properties. A study was undertaken to assess the effect of composition on α-Cr formation by varying the levels of Cr and Nb in the alloy. Each alloy was given the following four thermo-mechanical treatments: direct age, solution and age, solution and age, and age plus cold worked reductions of 10% and 20%. Samples were heat treated for 500, 1000 and 2000 hours at 649°C. Microstructural evaluations by light optical microscopy, SEM and XRD of extracted particles were performed and α-Cr formation was found to be dependent on both chemistry and processing conditions. In addition, impact properties were found to correlate with precipitation and growth of α-Cr.

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RELATIONSHIP OF MICROSTRUCTURE WITH MECHANICAL PROPERTIES OF ALLOY 625, 718 AFTER LONG TERM EXPOSURE: *Xishan Xie*[1]; [1]University of Science and Technology Beijing, High Temperature Alloy Division, Dept. of Mats. Sci. and Eng., Beijing 100083 P.R. China

Microstructures and phase transformations of the world-wide most used superalloy Alloy 718 at high temperatures(593 -704°) very long time exposure (til to 50,000 hours) was investigated by means of transmission electron microscope analyses and the relevant mechanical properties were also determined for the evaluation of strengthening and brittleness. The degradation of strengthening are concluded on the following three main reasons: 1. The coarsening of separately precipitated strengthening phases of gamma-double prime and gamma-prime; 2. The phase transformation of gamma-double-prime to stable delta phase with large plate-like morphology; 3. The formation of brittle sigma phase. Detail microstructure analyses of Alloy 625 at 1100F-1400F up to 10,000 hours were also studied using SEM, TEM. The experimental results show that the reduction of impact energy is attibuted to the precipitation of M6C type carbides and alpha-Cr particles along and within grain boundaries during long term exposure in alloy 625.

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LONG-TERM THERMAL STABILITY OF THERMO-SPAN ALLOY: *R. B. Frank*[1]; [1]Carpenter Specialty Alloys, Cartech R&D Center, P.O. Box 14662, Reading, PA 19612-4662 USA

Thermo-Span is an age-hardenable, Ni-Co-based superalloy that combines low thermal expansion characteristics with improved oxidation resistance compared to previous controlled-expansion superalloys. Heat-treated samples were exposed for 1500 hours at temperatures ranging from 900°F to 1250°F. Evaluations included tensile tests at room temperature, 1100°F and 1200°F, stress-rupture tests at 1250°F and post 1150°F creep tensile tests at 1150°F. The results showed that Thermo-Span alloy exhibits stable tensile properties and microstructures after 1500-hour exposures at temperatures within the range of 900°F and 1200°F. No embrittlement occurred at these temperatures. Exposures at 1250°F reduced strength but did not degrade stress-rupture properties. Neither stressed or un-stressed exposures at 1150°F had a significant effect on tensile properties at 1150°F.

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CREEP-RUPTURE OF ALLOY 718 AFTER THERMAL AGING UP TO 50,000 H: *Gary E. Korth*[1]; [1]Lockheed Martin Idaho Technologies Company, Metals and Ceramics, P.O. Box 1625, Idaho Falls, ID 83415-2218 USA

Alloy 718 given the conventional 718/621ϒC age-hardening treatment was thermally aged at 593, 621, and 649ϒC for times up to 50,000 hours. These temperatures bracket the lowest of the duplex age-hardening temperature. Subsequent creep-rupture tests conducted at the same temperature of thermal aging show 593ϒC aging to be beneficial up to 10,000 h and only slightly detrimental after 50,000 h. Material aged for 50,000h and tested at 621ϒC shows the rupture life to be approximately 60-65% of the unaged material, but at 649ϒC the aged material rupture life is of the order of 15% of the unaged material. Room temperature tensile properties of the aged material will also be presented with some microstructure evolution with the long-term aging.

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EFFECT OF THERMAL AGING ON MICROSTRUCTURE/COMPOSITION AND MECHANICAL PROPERTIES IN ALUMINIZED CoCrAlY COATINGS: *Jun Kameda*[1]; Tamra E. Bloomer[1]; Yuji Sugita[2]; Akihiro Ito[2]; Shigeo Sakurai[3]; [1]Iowa State University, Metallurgy and Ceramics, Ames Laboratory, 206 Metals Development Bldg., Ames, IA 50011 USA; [2]Electric Power R&D Center, Chubu Electric Power Co., 20-1 Kitasekiyama, Aza Otaka, Midori-ku, Nagoya 458 Japan; [3]Hitachi, Ltd., Mech. Eng. Research Laboratory, 3rd Dept., 1-1 Saiwaicho 3-Chome, Hitachi 317 Japan

The effect of thermal aging at 870ϒC for 8000 h in air on the microstructure/composition and mechanical properties (RT and 870ϒC) has been studied in aluminized CoCrAlY coatings consisting of four layered structure (region I-IV) of advanced gas turbine blades. Thermal aging led to a little oxidation/nitridation and a decrease in the Al content in a near surface region I. In a coating region II, coarse Cr rich σ precipitates formed during the thermal aging. Thermally aged internal (III) and near interface (IV) coating regions showed extensive dispersion of σ and/or Al/Ni rich β/α eutectic precipitates. Small punch tests at RT and 870ϒC in air have shown that the coating regions I and II of unaged and aged blades indicated easier formation of brittle cracks regardless of the composition change. The ductility of the regions III and IV at RT and 870ϒC, and the low cycle fatigue life of the region III were reduced by the thermal aging. The mechanical degradation at elevated temperatures in the aged coating regions III and IV is elucidated by taking into account the microstructure/composition evolution and environmental oxidizing effects. This work was supported by USDOE, Office of Basic Energy Sciences, Div. of Materials Science under contract no. W-7405-ENG-82.

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DEGRADATION OF MICROSTRUCTURE OF NICKEL SUPERALLOY <001> SINGLE CRYSTALS UNDER THE INFLUENCE OF TEMPERATURE AND/OR STRESS.: *Bakhteeva Natalia Dmitrievna*[1]; *Petrova Sofya Nikolaevna*[1]; Vinogradova Nina Ivanovna[1]; [1]Instittute of Metal Physics, Ural Branch of Russian Academy of Sciences, 18 S.Kovalevskaya Str., Ekaterinburg GSP-170, Sverdlovsk Region 620219 Russia

The microstructure of <001> single crystals of richly alloyed nickel superalloy containing 65% volume fracture of gamma-prime phase subjected to crystallization, heat treatment, tests for high-temperature creep and subsequent heatings has been investigated by various methods: metallography, electron microscopy and X-raying. The degradation of microstructure (intermetallide and carbide phases) has been revealed under the action of temperature and/or stress. The stability of lamellar gamma/gamma-prime structure at high-temperature heating was studied. The tight correlation is shown to exist between the morphology of gamma-prime particles and the high-temperature properties of single-crystal samples.

MANUFACTURING ISSUES IN RAPID THERMAL PROCESSING: Session II

Sponsored by: Electronic, Magnetic and Photonic Materials Division, Thin Films and Interfocus Committee

Program Organizers: N.M. Ravindra, New Jersey Institution of Technology, Dept. of Phys., Newark, NJ 07102 USA; Daniel F. Downey, Varian Ion-Implant System, Gloucester, MA 01930 USA; Anthony T. Fiory, Lucent Technologies, Bell Labs., Room 1D468, Murray Hill, NJ 07974-0636 USA; Steven D. Marcus, AST Elektronik USA Inc., Tempe, AZ 85284 USA; B. Sopori, National Renewable Energy Laboratory, 1617 Cole Blvd., Golden, CO 80401 USA

Wednesday PM Room: 14A
March 3, 1999 Location: Convention Center

Session Chair: Steven D. Marcus, STEAG-AST Elektronik, Tempe, AZ 85284 USA

2:00 PM KEYNOTE
THE APPLICATION OF RAPID THERMAL PROCESSING TECHNOLOGY TO THE MANUFACTURE OF INTEGRATED CORCIOTS=AN OVERVIEW: Alan Bratschun; SEMATECH

Like many of the technologies used to process integrated circuits, the road to manufacturing for RTP has been twisted. What began as a speculative laboratory apparatus, has evolved into a cornerstone of IC technology. Qualities that make RTP desirable for IC manufacture include the ability to process wafers individually, the ability to minimize the time wafers spend at elevated temperature, the convenience of clustering RTP to other systems, and the possibility of maintaining cold reactor walls. This paper will review how these properties make RTP desirable. The paper will also present an overview of the difficulties surrounding the use of RTP and describe how many of the serious hurdles have been overcome. It will summarize the evolution of RTP from a curiosity to a mainstay technology in building integrated circuits. It will then describe SEMATECH's role in working with RTP, ending with a direction for future applications of RTP based on the SIA Roadmap for semiconductors.

2:30 PM INVITED PAPER
CONTROL OF INTERFACE PROPERTIES OF Si-Al CONTACTS USING OPTICAL PROCESSING: *Bhushan Sopori*[1]; Wei Chen[1]; [1]National Renewable Energy Laboratory, 1617 Cole Blvd., Golden, CO 80401 USA

Control of the interface properties is important in making semiconductor-metal contacts with desirable properties. Fabricating contacts on solar cells poses unique challenges because they necessitate control of both their electronic and optical properties. This paper describes how Optical Processing can be applied to fabricate Si-metal contacts that satisfy both optical and electronic properties for solar cells. This process allows one to control the thickness of the semiconductor-metal melt during the contact formation, producing an abrupt Si-Al contact of very low contact resistivity and high optical reflectance. In addition, the contacts with a gradient in the Al concentration can be fabricated. We will also discuss the properties of Si-Al interfaces formed under various process conditions. Of particular interest are the reflection behavior and the formation of the P/P+ interface for high-efficiency silicon solar cells. We will show the measured optical and spreading resistance data and compare it with theoretical results.

3:00 PM INVITED PAPER
WAFER TEMPERATURE MEASUREMENT IN A RAPID THERMAL PROCESSOR WITH MODULATED LAMP POWER: *A. T. Fiory*[1]; B. Nguyenphu[2]; [1]Bell Laboratories, Lucent Technologies, Inc., Murray Hill, NJ 07974 USA; [2]Lucent Technologies, Inc., Microelectronics Group, Orlando, FL 32819 USA

Wafer temperature measurements similar to Accufiber's ripple technique were employed in a pyrometer to compensate for variable wafer back side emissivities. Power to the heating lamps was modulated with oscillatory functions of time. Fluctuating and quasi-steady components in detected radiation were analyzed to suppress background reflections from the lamps and to correct for effective wafer emissivity. Wafer process results for unpatterned wafers, as film thickness for thermal oxidation and as sheet resistance for annealing of high-dose shallow implants, were used to inter wafer4o-wafer process temperature variability over a range in back side emissivity. Emissivities were varied by depositing or growing one or more layers of silicon dioxide, silicon nitride, or polycrystalline silicon on the backsides.

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CALCULATION OF THE EMISSIVITY OF Si WAFERS: *Bhushan Sopori*[1]; Wei Chen[1]; Jamal Madjdpour[1]; N. M. Ravindra[2]; Sufian Abedrabbo[2]; [1]National Renewable Energy Laboratory, 1617 Cole Boulevard, Golden, CO 80401 USA; [2]New Jersy Institute of Technology, Dept. of Physics, Newark, NJ 07102 USA

This paper will discuss a computer-software for calculating the emissivity of silicon wafers of any surface morphology, for a given temperature and dopant concentration. The calculations use an optical model that includes surfaces of any shape - planar, rough, or textured. The optical constants, i.e. refractive index and absorption coefficient, are calculated as a function of temperature using an empirical model for an indirect bandgap semiconductor. We will compare the results of this model with other methods of emissivity calculations and with the experimental data. This software can be very useful for monitoring wafer temperature in RTP systems.

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TEMPERATURE UNIFORMITY OPTIMIZATION FOR A SILICON IMPLANT ANNEAL INTO GAAS USING OPUS♦ SIMULATION SOFTWARE: *Helmut Francz*[1]; Zaid Farukhi[1]; Steven D. Marcus[1]; Andreas Tillrnann[2]; Juergen Niess[3]; [1]Motorola, CS-1, Tempe, AZ 85284 USA; [2]STEAG AST Elektronik, Gambh, Dornstadt Germany; [3]STEAG AST Elektronik, Tempe, AZ 85284 USA

OPUS♦, which stands for "Optimized Uniformity Simulator", has been described in the literature as a powerful tool to assist in the optimization of temperature uniformity on the STEAG AST Elektronik series of rapid thermal processors. Historically, this tool, OPUS™, has been used extensively for a variety of silicon processing.

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THE APPLICATION OF RAPID THERMAL PROCESSING TECHNOLOGY TO THE MANUFACTURE OF INTEGRATED CIRCUITS-AN OVERVIEW: *Alan Bratschun*[1]; [1]SEMATECH

Like many of the technologies used to process integrated circuits, the road to manufacturing for RTP has been twisted. What began as a speculative laboratory apparatus, has evolved into a cornerstone of IC technology. Qualities that make RTP desirable for IC manufacture include the ability to process wafers individually, the ability to minimize the time wafers spend at elevated temperature, the convenience of clustering RTP to other systems, and the possibility of maintaining cold reactor walls. This paper will review how these properties make RTP desirable. The paper will also present an overview of the difficulties surrounding the use of RTP and describe how many of the serious hurdles have been overcome. It will summarize the evolution of RTP from a curiosity to a mainstay technology in building integrated circuits. It will then describe SEMATECH's role in working with RTP, ending with a direction for future applications of RTP based on the SIA Roadmap for semiconductors.

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RAPID PHOTOTHERMAL PROCESSING IN SEMICONDUCTOR MANUFACTURING IN THE 21ST CENTURY: *R. Singh*[1]; V. Parihar[1]; K. F. Poole[1]; [1]Clemson University, Department of Electrical and Computer Engineering, Center for Silicon Nanoelectronics, Clemson, SC 29634-0915 USA

Abstract Not Available.

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EMISSIVITY MEASUREMENTS AND MODELING OF INFRARED TRANSPARENT MATERIALS: *Manish Babladi*[1]; Oktay Gokce[1]; F. M. Tong[1]; Daniel E. Pierce[2]; Gyuido Guazzoni[3]; N. M. Ravindra[1]; [1]New Jersey Institute of Technology, Newark, NJ USA; [2]William Peterson University, Wayne, NJ USA; [3]US Army, CECOM, Fort Monmouth, NJ USA

Experimental results of the temperature dependent radiative properties of infrared transparent materials (quartz, lucalox and sapphire) have been reported in this study. These measurements have been performed using a spectral emissometer operating in the wavelength range of 0.8 to 20 microns and the temperature range of 17 to 900 ^{0}C. For double side polished materials, the measured optical properties have been deconvoluted to yield fundamental optical constants. Comparisons of the obtained results are made with those available in the literature. Applications of this study to rapid thermal process systems have been identified and explained.

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EFFECT OF ULTRAVIOLET (UV) AND VACUUM ULTRAVIOLET (VUV) PHOTONS IN RAPID PHOTOTHERMAL PROCESSING: *V. Parihar*[1]; R. Singh[1]; K. F. Poole[1]; A. Rohatgi[2]; [1]Clemson University, Department of Electrical and Computer Engineering, Center for Silicon Nanoelectronics, Clemson, SC 29634-0915 USA; [2]Georgia Institue of Technology, School of Electrical Engineering, Atlanta, GA 30322 USA

Abstract Not Available.

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APPLICATION OF SPECTRAL EMISSOMETRY FOR THE ESTIMATION OF CONDUCTION INTRABAND TRANSITIONS IN n AND p SILICON: *S. Abedrabbo*[1]; J. C. Hensel[1]; A. T. Fiory[3]; N. M. Ravindra[2]; [1]New Jersey Institute of Technology, Newark, NJ USA; [1]Kearfott Guidance and Navigation Corporation, Wayne, NJ USA; [3]Bell Laboratories, Lucent Technologies, Murray Hill, NJ USA

n-Si exhibits an absorption band in the wavelength range of 1-5 mm that is attributed to transitions of electrons from conduction band minima to the next higher band. This has been reported first by Spitzer and Fan for various doping concentrations ranging from 10^{14} – 10^{19} cm^{-3} at room temperature. It has been reported also that p-Si does not exhibit aa similar band structure in the extrinsic regime. In this work the first detailed temperature dependent conduction intraband transitions are reported as function of wavelength for p-Si in its intrinsic regime. The band peak has shown negligible dependence on temperature as expected and remains at l~2.3mm, while the peak intensity has risen as the temperature is increased indicating an increase in the thermally generated electrons ready to make the transition.

MATERIALS PROCESSING FUNDAMENTALS: Ferrous

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

Wednesday PM Room: 5A
March 3, 1999 Location: Convention Center

Session Chairs: Janusz Majta, University of Mining and Metallurgy, Dept. of Metall. and Mats. Sci., Krako 30-059 Poland; Derek O. Northwood, Ryerson Polytechnic University, Dept. of Eng. & Applied Sc., Toronto, Ontario M5B2K3 Canada

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ISOTHERMAL NORMALIZING SYSTEM BY UTILIZING THE RESIDUAL FORGED HEAT IN ALLOY CARBURIZING PRODUCTS: *Zhenbo Zhao*[1]; Cheng Liu[2]; Yunxu Liu[2]; *Derek O. Northwood*[3]; [1]University of Windsor, Mechanical & Materials Engineering, 401 Sunset Ave., Windsor, Ontario N9B 3P4 Canada; [2]Jilin Institute of Technology, Materials Engineering, 76 Yanan Dalu, Changchun, Jilin 130012 P.R.China; [3]Ryerson Polytechnic University, Engineering & Applied Science, 350 Victoria Street, Toronto, Ontario M5B 2K3 Canada

The processes and equipment for INURFH (Isothermal Normalizing by Utilizing the Residual Forged Heat) of alloy carburizing steel products are presented. It is shown that the four key parameters: namely (I) cooling rate before isothermal normalizing; (II) the lowest cooling temperature before isothermal normalizing; (III) isothermal temperature ; and (IV) isothermal time, should be controlled in order to meet the requirement of the isothermal normalizing treatment. The prediction and calculation of these parameters can be achieved on the basis of components treated and the technical requirements of steel parts by an on-line expert system for this isothermal normalizing system. It is believed that cost-reduction due to the energy savings resulting from this system for automobile parts heat-treatment is most promising.

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MICROSTRUCTURE AND CRYSTALLORGRAPHIC TEXTURE OF STRIP-CAST 4.3WT% SILICON STEEL SHEET: *Jae Young Park*[1]; Kyu Hwan Oh[1]; Hyung Yong Ra[1]; [1]Seoul National University, Division of Materials Science and Engineering, Shirim-dong 56-1, Kwanak-ku, Seoul 151-742 Korea

Grain oriented silicon steels have been mainly manufactured by continuous casting, hot rolling, cold rolling and recrystallization. In comparison to these conventional processes, the manufacture of grain oriented silicon steels by the strip casting process has several kinds of merits such as the omission of making progress and the increasement of silicon content etc., but because the hot rolling process is bypassed, through-the-thickness variation of texture is different with that of the hot-rolled sheet. In this report, Fe-4.3wt%Si steel sheet was prepared by the vertical type twin roll strip casting process and then the microstructure and texture at each thickness level of the strip were studied by optical metallography and quantitative X-ray texture analysis. The inhomogeneity of the texture and the microstructure through the sample thickness was investigated in the twin roll strip cast steel sheet.

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EVOLUTION OF NON-METALLIC INCLUSIONS IN ALUMINIUM KILLED LOW ALLOYED STEEL: *Rob Dekkers*[1]; *Bart Blanpain*[1]; *Patrick Wollants*[1]; *Frank Haers*[2]; *Carina Vercruyssen*[2]; *Leo Peeters*[2]; [1]Katholieke Universiteit Leuven, Metalllurgy and Materials Engineering, W. de Croylaan 2, Leuven, Vlaams Brabant B-3001 Belgium; [2]Sidmar N.V., Steel plant, J.F. Kennedylaan 51, Gent, Oost Vlaanderen B-9012 Belgium

Non-metallic inclusions in liquid steel are mainly formed during killing and cooling. As far as these particles are not captured by the slag, they are found in the cast steel where they can deteriorate the mechanical properties. In almost all cases inclusions disturb the continuous casting process, affecting thus directly the quality of the steel and the production capacity. Steel pin samples from the Sidmar plant (Belgium) were taken before, during and after killing/alloying of the steel in the ladle, after correction/alloying stage in the ladle and in the tundish. Also slab samples were studied. All samples concern the same type of aluminium killed low alloyed steel. The non-metallic inclusions were isolated from the steel matrix and investigated with scanning electron microscopy (SEM) and energy dispersive spectrometry (EDS). The evolution of the non-metallic inclusions is described by their number, size, shape and elemental composition. The main non-metallic inclusions present are aluminium oxides and spinel type compounds. Decrease of the amount of small (less than 1 μm) spherical inclusions during the process is related to coalescence of inclusions, which is illustrated by a counting methodology and by SEM micrographs.

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COMPUTER MODELING FOR TEXTURE DEVELOPMENT IN COLD ROLLED FERRITE: Guanglei Liu[1]; *Ruoju Zhang*[2]; [1]The University of Hong Kong, Dept. of Mechanical Engineering, Pokfulam Rd. Hong Kong; [2]The University of Hong Kong, Dept. of Electrical & Electronic Engineering, Pokfulam Road, Hong Kong

Microstructural investigation has shown that grain splitting or deformation banding develops progressively with increasing strains during cold rolling. Of particular significance to simulating texture development in rolled ferrite is the occurrence of deformation banding in the rolling plane since this allows another degree of freedom. Deformation Banding (DB) model includes DB in the rolling plane and applies the Relaxed Constraints (RC) mechanism for other shears, this gives an improved fit between experiment and theory within Taylor-Chin framework. The predicted texture with DB model and { 110 } + { 112 } slip systems is in good agreement with experimental observation. DB modeling is able to predict the evolution of specific textural features in cold rolled pure iron, especially, from different initial textures.

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RELATIONSHIP OF HOT DEFORMATION CONDITIONS TO MICROSTRUCTURE DEVELOPMENT IN TWO-PHASE REGION OF MICROALLOYED STEEL: *Anna K. Zurek*[1]; Janusz Majta[2]; [1]Los Alamos National Laboratory, MST-8, MS:G755, Los Alamos, NM 87454 USA; [2]University of Mining and Metallurgy, Metallurgy and Materials Science, al. Mickiewicza 30, Krakow 30-059 Poland

Most of the metal forming processes is performed in conditions where finish deformation temperature occurs in austenite region. However, it is well established that new very attractive possibilities of properties can be obtained when final product has a structure that came from deformation performed in two-phase region. In such produced steels, the main problem that should be solved is good inhomogeneity control of microstructure and resulted mechanical behaviors for metal forming operations. It is well known, that most effective and powerful tool to control such complicated deformation conditions is the computer modeling. In this paper a model of thermomechanical behavior and microstructural development during hot compression of microalloyed steel will be presented. We will test several conditions, for hot compression tests, at a number of strain rates of deformation of steel. Finally, a new concept of phase transformation model verified by the above experimental data will be introduced.

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IN-SITU OBSERVATION OF THE RATE OF DENITOROZATION OF MOLTEN STEEL: Muneyuki Iwasaki[1]; Takashi Ikeda[1]; *Masafumi Maeda*[1]; [1]University of Tokyo, IIS, 7-22-1 Roppongi, Minato, Tokyo Japan

Mass spectroscopy was used for the direct observation of the rate of denitrization. Nitrogen molecules or atoms were detected by a mass spectrometer set above the melt. Continuous monitoring of the intensity of the fixed mass number reflected the transfer of nitrogen from the melt to the vacuum. Direct observation enabled to study the rate of denitrization. The results of that with those by conventional the quench, sampling and chemical analysis technique agreed.

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KINETIC STUDY OF THE REDUCTION OF MnO SLAGS AND THE CARBON DISSOLUTION IN Fe-Mn BATHS.: José Roberto de Oliveira[1]; *Jorge Alberto Soares Tenório*[1]; [1]University of São Paulo, Metallurgical and Materials Dept., Av. Prof. Mello Moraes 2463, Butantã, São Paulo 05508-900 Brazil

In a smelting reduction process the reduction reaction occurs predominantly in the liquid state. The main reduction agent is the carbon from the carbon saturated iron bath. The aim of the present work was to determine the velocity equation and the mass transfer coefficient of the reduction rate of MnO content in a MnO-SiO2-FeO slag by iron saturated carbon and the carbon dissolution rate in a Fe-Mn bath. The manganese content in the iron bath was in the range of 5 to 40 wt.%. It was observed that the rates of carbon dissolution in all Fe-Mn baths are faster than the rates of MnO reduction by the carbon saturated liquid iron.

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OPTICAL PYROMETRY IN METALLURGY AND IN PHYSICAL METALLURGY - SOME NEW THEORETICAL AND EXPERIMENTAL RESULTS: Evgeny D. Glazman[1]; [1]3T - True Temperature Technology, Theradion Industrial Park, Misgav 20179 Israel

In this work we describe a new approach to the problem of non - contact measurement the true thermodynamic temperature of fluid and solid materials in industrial processes. Based on this technique, an optical system for the measurement of the actual temperature was designed. The main advantage of the specified multispectral method is the ability to give an information about the true radiating efficiency (emissivity) of the measured object surface, together with the information about the brightness and color temperature. The indicated system is widely applicable to variety of industrial processes for measurement the temperature of fluid steel, aluminum and aluminum alloys, copper, nickel, cobalt and other materials being in liquid or solid state. The high accuracy of the system was demonstrated to give a reading error not greater than ± (1º1.5%). Amongst the industrial process applications of the system are: Blast furnace of fluid steel, continuous casting and rolling of steel and aluminum, nickel and cobalt melts, as well as extrusion processes of aluminum and its alloys [1]. The Introduction of the new pyrometer to industrial use allows not only to solve the problem of non-contact true temperature measurement of high temperature processes, but also to efficiently combine it with complex and automatic control systems. References: 1. E.D. Glazman, Measurement of Thermodynamic Temperature in the Extrusion Process of Aluminum and Aluminum Alloys, Light Metal AGE, 46-8, April 1998.

MICROMECHANICS AND MICROMECHANISMS OF DEFORMATION AND FRACTURE: A SYMPOSIUM IN HONOR OF PROFESSOR ALI S. ARGON: Ali S. Argon Symposium VI

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

Wednesday PM Room: 14B
March 3, 1999 Location: Convention Center

Session Chairs: Robert O. Ritchie, UC-Berkeley, Dept. Mat. Sci. & Mineral Eng., Berkeley, CA 94720-1760 USA; J. G. Williams, Imperial College of Science Technology & Medicine, Dept. of Mech. Eng., London SW7 2BX UK

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ANALYZING CUTTING VIA FRACTURE MECHANICS: *J. G. Williams*[1]; [1]Imperial College of Science, Mechanical Engineering Department, Technology and Medicine, Exhibition Road, London, SW7 2BX UK

Cutting a strip with a blade or wedge is used to assess the fracture toughness of many systems. It can be used for cleaving layers as in mica or in breaking adhesive joints. A very similar mechanism is involved in cutting layers as in microtomes or planes. In all these cases energy is dissipated in friction and plastic work as well as fracture. The plastic work gives curling of the strip and this provides a method of determining the plastic work. Friction can be measured from blade forces. This paper will describe an analysis scheme to correct the data for both friction and plastic dissipation, so that the true fracture energy can be found. Examples will be given for adhesives and the cutting of polymers and biological samples.

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PREDICTING CLEAVAGE CRACK GROWTH IN BCC POLYCRYSTALS: *Frank A. McClintock*[1]; [1]Massachusetts Institute of Technology, Department of Mechanical Engineering, Room 1-304, Cambridge, MA 02139-4307 USA

A preliminary model of polycrystalline cleavage was based on square cylinders normal to the macrocrack. Each cylinder was randomly assigned one of five cleavage orientations. The linkage of cracks was assumed to occur by shear sliding off and cracking along the grain boundaries. Approximate hand calculations gave an extremely tortuous crack path, as observed fractographically. The height differences that developed gave a work per unit area comparable to the lower shelf value for initial macro-crack growth. Here, after a review of the fractographic literature, possible extensions of the model are explored. Hexagonal cylinders, even with only one tilt angle, involve some dozen different tilt-twist misorientations across grain boundaries. For any one grain-to-grain penetration of cleavage into a neighboring grain, calculation of the driving paramaters and resistance functions would involve a multi-scale calculation. The scales involved range from the atomic to the grain-sized boundary conditions on the inhomogeneous polyslip in the grain being penetrated. For small twist angles, multiple initiation sites result in river patterns. These difficulties led to quantifying the square-cylinder model to study the effects of the length of, and the initial roughness along, the polycrystalline crack.

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MICROMECHANICAL MODELLING OF THE PLASTIC BEHAVIOR AND DAMAGE NUCLEATION OF A DUPLEX STAINLESS STEEL: *Jacques Besson*[1]; Stephane Bugat[1]; Anne-Francoise Gourgues[1]; Andre Pineau[1]; [1]Ecole des Mines de Paris, Centre des materiaux CNRS UMR 7633, BP 87, Cedex, Evry 91003 France

Ductile rupture is frequently initiated in second phase particles. A micromechanical description of damage nucleation therefore requires an estimation of strains and stresses in the different phases. In the present study, this approach is applied to a duplex stainless steel in which the ferritic phase is embrittled by a phenomenon known as "475°C embrittlement". Consequently, the hardness of the ferritic phase increases and induces a significant decrease of ductility and fracture toughness. The investigated duplex steel consists of large ferrite grains of about 10~mm formed during the early stages of solidification. As cooling proceeds, austenite grains (size 1~mm) are formed in the ferrite according to the Kurdjumov - Sachs relationships. These grains are defined as areas where the austenitic phase keeps the same crystallographic orientation. Both phases are interconnected and percolated and form laths whose spacing equals 10~microns. As cleavage is primarily controlled by tensile stresses, any attempt to model damage nucleation should be based on a realistic estimation of the local stress and strain fields. This study is motivated by the fact that damage is heterogeneous; highly damaged zones correspond to some austenitic grains evidencing the role of crystallography in the damage process. Damage rate is affected by the orientation of the ferrite with respect to both the macroscopic load and the surrounding austenite. A micromechanical model, accounting for crystal plasticity, has been developed to represent average stresses and strains in both phases over a representative volume element corresponding to the interconnected network. This model is used to simulate, using the Finite Element Method, small tensile samples tested in a Scanning Electron Microscope. Local grain orientations are measured before testing using Electron Back Scattering Patterns. They are used as input for the simulation. Comparison of computed stresses in the ferrite with observed damage nucleation, allows to derive a cleavage criterion relative to the ferrite only and independent of the local crystallographic orientations.

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THE THEORETICAL STRENGTH IN SHEAR: C. R. Krenn[1]; D. Roundy[2]; M. L. Cohen[2]; *J. W. Morris, Jr.*[1]; [1]University of California, Department of Materials Science, Berkeley, CA 94720 USA; [2]University of California, Department of Physics, Berkeley, CA 94720 USA

The theoretical shear strength of a material is defined as the shear stress a defect-free specimen can withstand before unstable deformation. It is, therefore, the ultimate measure of hardness and the most fundamental indication of mechanical properties. While theorists have attempted estimates of the theoretical shear strength for many years, it has recently become possible to compute it through ab initio electronic structure calculations, using the local density approximation, with full atom relaxation. Results will be presented for several prototypic elements and compounds. The results include the energy-strain and shear stress-strain curves for shear displacement to instability, the atom displacement paths, and the evolution of the electronic structure, which helps to explain whythe theoretical strengths have the values they do.

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FRACTURE AND FATIGUE OF BULK AMORPHOUS METALS: Christopher J. Gilbert[1]; Valeska Schroeder[1]; *Robert O. Ritchie*[1]; [1]University of California, Berkeley, Materials Science and Mineral Engineering, 463 Evans Hall #1760, Berkeley, CA 94720-1760 USA

The fracture and fatigue properties of the bulk metallic glass alloy, $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ (at.%), are characterized with specific emphasis on controlling microstructural mechanisms. It is found that the fully amorphous alloy exhibits a high fracture toughness of ~55 MPa m, although rounded-notch Charpy impact energies are less than 10 J. Moreover, the K_{Ic} toughness is markedly sensitive to strain rate and the level of precrack damage, and shows no resistance-curve behavior. Under both quasi-static and dynanmic loading, fracture surfaces exhibit a characteristic vein morphology with apparent evidence for local melt-

ing during fracture. The latter is consistent with spectroscopy measurements of extremely high temperatures (>2000K) during fracture, associated with marked fracto-luminescence. This fracture mode is consistent with Argon and Salama's model of a variant of the Taylor instability, i.e., associated with the tendency of a "fluid" meniscus propagating under a positive pressure gradient to break up into a series of "fingers". In addition, upon crystallization the alloy becomes severely embrittled with K_{Ic} dropping to ~1 MPa m. Under cyclic loading, crack-propagation behavior in the amorphous structure is similar to that observed in traditional polycrystalline alloys, with alternating blunting and resharpening of the crack tip, as evidenced by striations on fatigue fracture surfaces. However, in sharp contrast, the (unnotched) stress-life properties are markedly different. Specifically, crack initiation occurs quite readily due to the lack of microstructural barriers which normally provide crack-arrest points; this results in a very low fatigue limit of ~1/25 of the tensile strength.

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COMPATIBILITY STRESSES AT GRAIN BOUNDARIES AND THEIR EFFECT ON CRACK INITIATION IN HIGH CYCLE FATIGUE: *Peter Neumann*[1]; [1]Max-Planck Institut fur Eisenforschung GmbH, Max-Planck-Str. 1, 10237 Dusseldorf Germany

The compatibility stresses at elastically incompatible grain boundaries are discussed and presented in analytical form. These incompatibility stresses give rise to a logarythmic singularity of stresses at the intersecting line between a grain boundary and the specimen surface. Approximate analytical solutions for these stresses are given based on the work of Mushkelishvili. Furthermore, some examples of three-dimensional calculations of stress-concentrations at grain boundaries are given. These theoretical results are compared with the observation of fatigue crack initiation experiments with copper and austenitic steel polycrystals. In the high cycle i.e. low plastic strain regime (cycles to failure>300,000) the initiation sites were found to be twin boundaries almost exclusively. By local orientation measurements at hundreds of grain boundaries quantitative estimates of local stress concentration were obtained and compared with the theoretical results. An almost one to one correlation was found between the occurrence of high local stress concentrations at twin boundaries and crack nucleation sites. Thus the compatibility stresses seem to be the main cause for fatigue crack initiation in high cycle fatigue, when other faults like inclusions are missing.

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WORKPIECE WEAR MECHANISMS IN DEFORMATION PROCESSING: Gilbert J. Baker[2]; *Roger N. Wright*[1]; [1]Rensselaer Polytechnic Institute, Materials Science and Engineering Department, 206 MRC Building, Troy, NY 12180 USA; [2]Essex Group, Inc., Fort Wayne, IN 46801 USA

Workpiece wear, as opposed to tool wear, has received little attention in deformation processing analysis, except perhaps for the relatively gross losses associated with sticking friction. This paper focuses on the subtle, but important, liberation of particles from the workpiece surface (sometimes called "fines"). Emphasis is placed on copper wire drawing, where "fines" are a major issue vis-a-vis lubrication, surface quality, and subsequent insulation application. Detailed laboratory study reveals that "fine" generation involves the classical mechanisms of delamination wear and rapid wear. In the case of copper wire drawing, delamination wear involves damage to the near-surface from prior processing. The rapid wear observed is consistent with a modified Archard equation. Delamination wear is retarded by the application of back tension, and rapid wear can be minimized by die angle optimization.

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MICROSTRUCTURE AND MECHANISMS OF CYCLIC DEFORMATION OF ALUMINUM SINGLE CRYSTALS AT 77K: *M. E. Kassner*[1]; [1]Oregon State University, Mechanical Engineering, Rogers Hall, Corvallis, OR 97331 USA

Aluminum single crystals were cyclically deformed in single slip at small strain amplitudes at 77K to presaturation. The dislocation substructure was analyzed in detail. The maximum dipole height suggests a strength approximately equal to the flow stress. The stress to move a dislocation through a dipole bundle is also calculated to be approximately equal to the flow stress. In situ cyclic reverse (shear) deformation experiments in the high-voltage transmission electron microscope (HVEM) were successfully performed using the X-Y technique where thin foils are stressed in alternating perpendicular directions. The experiments indicate that loops frequently expand from the dipole bundles into the channel and the edge component is absorbed by nearby bundles, leaving screw segments behind. The screw dislocations that span the channel move easily and reverse direction with shear reversal. There is no obvious evidence for internal backstresses that assist plastic deformation on reversal of the applied shear.

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

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

Wednesday PM Room: 11B
March 3, 1999 Location: Convention Center

Session Chairs: Hans Conrad, North Carolina State University, Dept. of Mats.Sci. and Eng., Raleigh, NC 27695-7907 USA; James C. M. Li, Rochester University, Dept. of Mech. Eng., Rochester, NY 14627 USA

2:00 PM INVITED PAPER

ADHESION AND PROGRESSIVE DEBONDING OF INTERFACES IN THIN FILM STRUCTURES: *Reinhold H. Dauskardt*[1]; [1]Stanford University, Dept. of Mats. Sci. and Eng., 416 Escondido Mall, Bldg. 550, Stanford, CA 94305-2205 USA

The reliability of microelectronic devices and their packages containing thin film structures is strongly influenced by the interfacial adhesion of the many resulting bimaterial interfaces. Further, delayed failure and lifetimes of devices may be dictated by progressive debonding along one (or more) interface. These fractures are driven by residual stresses, thermo-mechanical cycling and mechanical loading. Time dependencies reflect subcritical cracking enhanced by temperature (creep), moisture or corrosive species (stress corrosion), or even cyclic loading (fatigue). Long term reliability and life prediction must be addressed in terms of the above time dependent failure mechanisms. In this presentation, techniques that have been developed to accurately measure the interfacial fracture energy are described for interfaces found in multilayer thin film structures as well as in larger scale packaging structures. Unique time-dependent delamination data for debonding of Si02 interlayer dielectric films from Al lines in interconnect structures will be presented together with progressive debonding behavior of various polymer/metal interfaces measured under static and cyclic fatigue loading conditions. Time dependent delamination data is compared to critical adhesion values. Behavior is rationalized in terms of the salient subcritical debonding mechanism involving environmental interactions and even processes of classic fatigue. The effect of interface morphology, adjacent layer thickness, loading parameters and environment on delamination will be considered. Finally, implications for life prediction are discussed.

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IMPRESSION AND INDENTATION FATIGUE TESTING: *James C. M. Li*[1]; [1]University of Rochester, Mats. Sci., College of Arts, Sciences and Engineering, Rochester, NY 14627 USA

Fatigue experiments were done locally by an indenter to obtain information about the local material properties such as its anelasticity, plastic zone propagation and crack initiation. While under a static load a plastic zone develops but then stops, a cyclic load of the same magnitude can continuously propagate the plastic zone so that the indenter sinks to a steady rate. This steady rate can be affected by a few cycles of overloading or underloading. Generally a cycle of overloading to a higher load and then return to the original load, the initial rate is very low and it takes many cycles at the original load to return to the original state rate. A few cycles of underloading produces the opposite effect. This and the number of cylcles needed to initiate a crack and its relation to anelastic behavior will be reported. Work supported by NSF through DMR 9623808 monitored by Dr. Bruce MacDonald.

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INTERNAL FRICTION ASSOCIATED WITH SURFACE OXIDIZED LAYERS OF METALS: *Masahiro Koiwa*[1]; Osamu Yoshinari[2]; [1]Kyoto University, Dept. of Mats. Sci. and Eng., Sakyo-ku, Kyoto 606-8501 Japan; [2]Nagoya Institute of Technology, Department of Materials Science and Engineering, Showa-ku, Nagoya, Aichi 466 Japan

Internal frictions of metals are often measured by use of a torsion pendulum, the vibrational frequency being typically 1Hz. Since the strain is the largest at the surface of a specimen in a torsional mode, thin surface layers can contribute significantly to the observed internal friction. We have observed the oxygen Snoek peak associated with the surface oxidation of initially oxygen-free specimens of V, Nb and Ta. Some effects associated with the formation of oxide films have been reported for Fe and Co. Such effects of surface layers on the internal friction of metals will be reviewed.

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3:50 PM INVITED PAPER

DAMAGE CHARACTERIZATION OF COPPER/POLYMER CONSTRUCTIONS IN TENSILE, BENDING AND CYCLIC LOADINGS: *Douglas M. Shinozaki*[1]; Harish D. Merchant[2]; [1]University of Western Ontario, Department of Mech. Eng., London, Ontario N6A5B9 Canada; [2]Gould Electronics, 34929 Curtis Boulevard, Eastlake, OH 44095 USA

Thin copper foil, copper film or deposit on polyimide film, polyimide/copper/adhesive/polyimide multilayer and etched copper lines sandwiched symmetrically between the adhesive and polyimide layers are characterized. Following tensile, bending, or cyclic loading, several types of damage are observed: (i) strain localization in polyimide or copper, (ii) delamination between copper and adhesive layers, (iii) surface roughening and notching of copper, (iv) geometrical changes, specifically thinning or necking of copper and (v) edge cracking of copper lines when the line width to thickness ratio is about four or lower. The fatigue cracks originate on the free delaminated copper surface in the tensile strain field and propagate across the line width and through the line thickness. In roll fatigue, the fatigue cracks propagating though copper thickness are arrested at mid-thickness, change direction by 90 degrees and propagate across the line width, significantly enhancing the fatigue life. The cracks generally propagate along grain boundaries, finer grain structure providing a more torturous path for crack propagation.

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INTERNAL FRICTION OF SUPERCONDUCTING YBCO WIRES AT 200KHZ WITH IN SITU HEAT TREATMENT: *Masakuni Ozawa*[1]; M. Inagaki[1]; S. Suzuki[1]; [1]Nagoya Institute of Technology, Ceramics Research Lab, Asahigaoka, Tajimi 507 Japan

We developed a new instrument for the measurement of short wires with a dimension of ca.1mm diameter and 5-10mm length using piezoelectric effect of a LiNbO3 and SiO2 crystal at 100-300kHz. The system consists of impedance analyzer, controlling PC and a furnace. Piezoelectric d-matrix was determined by previous data of LiNbO3 and quartz. This method was applied to measure Young's modulus and internal friction (IF) of a superconducting polycrystalline YBa2Cu3O6+x (YBCO) wire which was subjected to in situ cyclic heat treatment at temperatures of 30-to-500C in air. Two IF peaks were observed, depending the oxygen content of samples. We determined an activation enthalpy and relaxation time of oxygen-site relaxation in YBCO crystal from IF data. This instrument will be applied to the elastic measurement of small ceramic, polymer and metal samples atca.100KHz in various temperature and atmosphere conditions.

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ANALYSIS OF THERMO-MECHANICAL INTERACTION IN MINIATURE SOLDER SYSTEM UNDER CYCLIC FATIGUE LOADING: *Bor Zen Hong*[1]; [1]IBM, Microelectronics Division, 1580 Route 52, Hopewell Junction, NY 12533 USA

Over the past decade, an effort aimed at improving the capability of complex lifetime analysis for miniature solder systems was motivated by a continuous surge of interest in developing reliable solder interconnection structures with applications to the higher I/0 and power density microelectronic packages. Such structures, in particular interest of solder bump type are the flip chip C4 (controlled chip connection collapse), BGA (ball grid array) and CGA (column grid array), could be exposed to various cyclic thermomechanical loads with resulting fatigue failure during manufacturing, test and use in service. Some of the critical lifetime analysis issues, on the macroscopic, microstructural and mesomechanical (interrelation between microstructure response and external loads exerting on the continuum scale of structure) scales, related to the thermo-mechanical interactions of solder systems include the difficulties associated with: (1) characterizing time-dependent, nonlinear deformation response and predicting fatigue life, (2) modeling and analyzing of various coupled and uncoupled thermo-mechanical interactions in the isothermal, adiabatic and anisothermal fatigue environments, and (3) simulating the transient, nonlinear thermal (heat transfer)-structural (thermal stress) response in a convectively-cooled packaging structure under power cycling. In this paper, the goal is set toward threefold and can be summarized as follows: (1) identification of the possible phenomena or mechanisms involved in thermo-mechanical interactions in solder system under cyclic fatigue loads, such as time-dependent deformation induced mechanical energy being transferred into heat and further leads to the counterparts of dissipated processes of viscous loss and thermal conduction loss, and vice versa, (2) literature review on the development of the constitutive models necessary for describing the time-dependent, nonlinear deformation for the tin-based solder alloys, such as lead-contained and lead-free, concentrated on the unified visc oplasticity theories based on internal variables (back or equilibrium stress and drag stress and (3) constitutive modeling with the selected viscoplasticity theories and finite element simulations for the selected examples of miniature solder systems under specific cyclic fatigue loads due to thermo-mechanical interactions.

NANOSTRUCTURED HYBRID MATERIALS: Characterization

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 Phy., 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

Wednesday PM Room: 16A
March 3, 1999 Location: Convention Center

Session Chair: Sara A. Majetich, Carnegie Mellon University, Dept. of Phys., Pittsburgh, PA 15213 USA

2:00 PM INVITED PAPER
STRUCTURAL, CALORIMETRIC, AND MAGNETIC STUDIES OF AMORPHOUS AND NANOCRYSTALLINE Co SUBSTITUTED Fe-Se-B-Nb-Cu AND Fe-Zr-B-Bu SOFT MAGNETIC MATERIALS: *Karl M. Unruh*[1]; [1]University of Delaware, Dept. of Phys. and Astronomy, Newark, DE 19711 USA

Co substituted Fe-Se-Nb-Cu and Fe-Zr-B-Cu alloys have been prepared by rapid quenching from the melt over a wide range of Fe/Co ratios. Subsequent thermal treatments have transformed the initially amorphous materials into a nanocrystalline sate characterized by a typical grain size of about 10 nm. The evolution of the magnetic properties of both the amorphous and nanocrystalline alloys have been studied form room temperature to above 800ϒC, and the saturation magnetization, Curie temperature, and coercivity determined as a function of the Fe/Co ratio. X-ray diffraction, electron microscopy, and calorimetric measurements have also been carried out and the microstructural information obtained from these studies has been correlated with the magnetic properties. The results of these measurements indicate that Co has indeed been incorporated into the nanocrystalline phase. The observation and the relative stability of the magnetically soft nanophases for temperatures near 400ϒC indicate that these alloys may be potentially useful as high temperature soft magnetic materials.

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DOMAIN BEHAVIOR IN MAGNETIC NANOSTRUCTURES AS REVEALED BY MOIF OBSERVATIONS: *Robert D. Shull*[1]; Alexander J. Shapiro[1]; Valerian I. Nikitenko[2]; Vladimir S. Gornakov[2]; [1]National Institute of Standards & Technology, Metallurgy Division, Bldg. 223, Rm. B152, Gaithersburg, MD 20899 USA; [2]Institute of Solid State Physics, RAS, Chernogolovka, Moscow Region Russia

A magneto-optical indicator film (MOIF) technique has been used for imaging magnetic domains and applied to magnetic nanostructures, including granular metals, magnetic multilayers, and antiferromagnet (AF)/ferromagnet (FM) bilayers. In this technique, the sample domains are imaged by their effect on a garnet film with in-plane magnetization located immediately above the sample. In addition to static domain structures, dynamic information has been obtained by monitoring the domain pattern evolution upon the application of an external magnetic field. Fractal type domain walls were observed in Co/Ag granular metals with a two-step remagnetization process, non-homogeneous nucleation processes were observed in AF/FM bilayers with remagnetization behavior dependent upon field direction, and non-collinear spin configurations were detected in Cu/Co multilayers (electrodeposited on Si substrates) displaying giant magnetoresistance (GMR) effects during the remagnetization process. In these latter samples, the GMR magnitude was correlated with the spin reorientation mechanism. In all samples the effects of crystal lattice defects on the remagnetization process was documented, and found to be significant. The MOIF technique was also found to be capable of detecting not only the domain structure of the surface layer, but also that of subsurface layers in a multilayer morphology. In this presentation, a review of the domain statics and dynamics which have been observed in a variety of nanostructured material types will be discussed. Particular attention will be given to the origin of enhanced coercivity in a bilayer system with unidirectional anisotropy.

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A DEPTH PROFILE STUDY OF THE STRUCTURE OF CHEMICALLY GROWN Cu FILMS ON AlN, AND ITS RELATION TO FILM PROCESSING : *Luz J. Martinez-Miranda*[1]; Yiqun Li[1]; Lynn K. Kurihara[2]; Gan Moog Chow[3]; [1]University of Maryland, Dept. of Mats. and Nuclear Eng., Bldg. 090 Rm 2135, College Park, MD 20742-2115 USA; [2]Naval Research Laboratory/Potomac Research International, Washington, D.C. 20375 USA; [3]Naval Research Laboratory, Washington, D.C. 20375 USA

We have studied Cu coatings grown on AlN substrates via a polyol deposition method using grazing incidence X-ray (GIXS) techniques and small angle scattering techniques to determine the dependence of film structure on depth as well as the presence of nanometer size structures in the films. Small angle measurements indicate the presence of ordered structures in the order of 4 nm close to the surface of the films. Depth studies using different X-ray energies in combination with the GIXS technique suggest the first 20 to 60 nm of the film correspond to a textured region, with strains ranging between +0.1% to -0.6%. The azimuthal ordering in the plane of the films depends on the sample deposition time and the substrate orientation. This work was supported partially by a NSF grant No. ECS-9710789, and by NRL and ONR nanostructured materials programs. X-ray studies were performed at the National Synchrotron Light Source at Brookhaven National Laboratory, which is supported by the U. S. Department of Energy.

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INTERDIFFUSION IN GRADED TiC-Ti MULTILAYERS.: Moshe Peter Dariel[1]; *Itzhak Dahan*[1]; Uri Admon[1]; Joseph Sariel[1]; Naum Frage[1]; [1]Ben-Gurion University, Mats. Eng., Beer-Sheva 84105 Israel

A functionally graded transition zone between a hard TiC coating and a ferrous metal substrate, e.g., a tool steel, can be formed by taking advantage of the stability range of the titanium carbide phase that extends from TiC0.5 to TiC. The transition zone is formed by sputter deposition of a multilayer stack of nanometric TiC and Ti layers. The composition gradient within the carbide layer is generated by varying the relative thickness of the as-deposited Ti and TiC layers within the stack. A subsequent short diffusion treatment eliminates the interfaces between the adjacent layers yet maintains an overall carbon composition gradient across the thickness of the coating. The relative thickness of the individual sputtered layers is adjusted to yield a low carbon composition in the coating close to the substrate and a stoichiometric composition near the external surface. The composition profile within the coating can be further optimized with respect to residual stresses that arise during cooling after the diffusion anneal. In this approach, interdiffusion between adjacent TiC and Ti layers is a crucial processing step. The design of the diffusion treatment parameters requires solving the diffusion equations in the graded multilayer. The relevant diffusion parameters were obtained by x-ray diffraction study of the structural evolution in a multilayer stack with uniform layer thickness, as a function of the temperature and the duration of the diffusion anneal. The effects of interdiffusion between the adjacent layers superpose on recrystallization processes occurring in the as-deposited layers. Noteworthy is also the large departure of the interdiffusion parameters in the sputter-deposited nanometric layers from values extrapolated from high temperature measurements in bulk material.

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4:00 PM INVITED PAPER
MECHANICAL AND TRIBOLOGICAL PROPERTIES OF SPRAY-COATED CONVENTIONAL AND NANOSTRUCTURED WC/Co

COMPOSITES: *Trautgott E. Fischer*[1]; L. Liu[1]; Y. Qiao[1]; [1]Stevens Institute of Technology, MSE, Castle Point on Hudson, Hoboken, NJ 07030-5991 USA

We review the hardness, toughness, adhesive and abrasive wear resistance of WC/Co composites. We briefly review these properties for sintered bulk cermets and the effect of the WC grain size and the benefit of nano structured materials. The hardness of cermets increases and their toughness decreases with decreasing cobalt mean free path. Nanostructured cermets (WC size 70 nm) further increase the hardness without detriment to toughness. Abrasive and sliding wear resistance increase with the hardness of the material, but nanocomposites show an additional increase in abrasion resistance. Coatings applied with the thermal spray method have lower hardness and wear resistance than bulk material because of the lower adhesion between splats. The wear mechanisms are also different, consisting of polishing in sintered materials and removal of splats in the coatings.

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NANOINDENTATION MEASURE OF ADHESION IN LAYERED NANOSTRUCTURES: *Natalia Tymiak*[1]; Nagaraja Rao[2]; Steven Girshick[2]; Joachim Heberlein[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]University of Minnesota, Mechanical Engineering, 111 Church St. SE, Minneapolis, MN 55455 USA

Processing-structure-adhesion relationships have been established for nanostructured SiC films on Mo. These films have been produced with the novel method of Hypersonic Plasma Particle Deposition (HPPD) which produces a nanostructured compact consisting of 10 nm to 50 nm size particles. In addition, application of the nanoscale thick W overlayers have been incorporated to enhance mechanical properties of the films thereby creating a metal-nanostructured ceramic composite. A bi-layer elastic analysis has been utilized to assess adhesion strength from the indentation induced delamination measurements. Constitutive properties of the SiC films required for the analysis have been evaluated with the nanoindentation method. Before-test and after-test imaging of an indented area was possible with a Hysitron nanoindenter. Combined with the SEM results, this allowed correlation of the film structure with the observed mechanical property gradients across the film thickness. Measured interfacial fracture toughness has been correlated to the near-substrate film structure as revealed by SEM cross-sectional analysis. Adhesion strength have been found to increase with the increasing substrate temperature which was identified as the most critical deposition parameter.

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NANOSTRUCTURED Ni COATINGS DEPOSITED BY THE POLYOL PROCESS: *Gan Moog Chow*[1]; S. H. Lawrence[2]; C. R. Feng[2]; [1]National University of Singapore, Mats. Sci., Kent Ridge 119260 Singapore; [2]Naval Research Laboratory, Mater. Sci. and Technol., Code 6323, Washington, DC 20375 USA

Nanostructured nickel coatings were deposited on copper substrates by reducing nickel acetate in refluxing ethylene glycol. This process has been used to prepare nanostructured composite powders and films. The Ni coatings were studied using x-ray diffraction, scanning electron microscopy, transmission electron microscopy, high resolution transmission electron microscopy, energy dispersive x-ray fluorescence spectrometry, and Vickers hardness testing. The average crystallite size and the morphology of the coatings were studied as a function of deposition time at a fixed concentration. The effects of heterogeneous nucleating aids were also investigated. The crystallite size was found to initially increase with deposition time, and then decrease at a longer deposition time. The crystallite size was reduced when the nucleating aids were employed. Microhardness data revealed softening for small crystallite size.

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CONTINUUM BASED MODELS OF INTERFACES IN NANOSTRUCTURED HYBRID COATINGS: *I. A. Ovid'ko*[1]; [1]Russian Academy of Sciences, Laboratory for Theory of Defects in Materials, Institute for Problems of Mechanical Engineering, Bolshoj 61, Vas. Ostrov, St. Petersburg 199178 Russia

This report reviews continuum based models of interfaces - intergranular and interphase boundaries - in nanostructured materials with the special attention being paid to specific peculiarities of interfaces in metallic and ceramic phases in nanostructured hybrid films and coatings. Interfacial defect structures as well stress-field and energetic characteristics of interfaces are considered. The nano-scale grain size effect in nanostructured hybrid films and coatings is discussed.

SURFACE ENGINEERING: SCIENCE AND TECHNOLOGY I: Solid Freeform Fabrication

Sponsored by: Materials Processing and Manufacturing Division, Surface Engineering Committee; Shaping and Forming Committee; Structural Materials Division, Structural Materials 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; John J. Moore, Colorado School of Mines, Golden CO 80401 USA; John L. Lombardi, Advanced Ceramic Research, Tuscon, AZ 85706-50113 USA

Wednesday PM Room: 7B
March 3, 1999 Location: Convention Center

Session Chairs: D. B. Chrisey, Naval Research Laboratory, Washington, D.C. USA; J. C. Arnault, Groue Surfaces-Inerfaces, Instut de Physique et Chimie de Straabourg France

2:00 PM

LASER ENGINEERED DIRECT FABRICATION/MANUFACTURING OF METALS: *John E. Smugeresky*[1]; D. M. Kelcher[2]; [1]Sandia National Laboratories, Livermore, CA 87123 USA; [2]Optomec Design Company, Albuquerque, NM 87123 USA

Direct Fabrication Technology, which utilizes computer aided design (CAD) solid models to automatically produce functional piece parts, is rapidly gaining popularity as a means to significantly reduce the time to market of new products. Since the introduction of stereolithography in 1982, several Rapid Prototyping (RP) technologies have evolved. These RP technologies rely almost exclusively on the use of surrogate rather than actual materials of construction to create models as an intermediary step to impact the manufacturing process. These models provide a means for designers to quickly realize their designs and also provide reasonable patterns for processes such as castings. Unfortunately, these models produced on RP systems are typically constructed from polymers or other low strength materials that do not allow them function in very demanding situations. Based on the successes of these early RP methods, researchers have more recently begun to develop laser-based methods to obtain fully dense metallic components directly from a CAD solid model thus eliminating intermediary processing steps. These laser-based methods have demonstrated that near-net-shaped components can be fabricated directly from a CAD solid model in a variety of useful materials. Furthermore, components fabricated using these techniques exhibit material properties equal, or superior to those of similar composition components fabricated using conventional methods. Many of these methods hold a great deal of promise for revolutionizing the approach to manufacturing. Although systems to apply this technology are currently research based, efforts are underway to bring this technology to the commercial manufacturing floor. In this article, an overview of the current state of Laser Engineered Direct Fabrication/Manufacturing technologies is given, demonstrating we may be closer to acceptance of these technologies as a preferred method of manufacture than is commonly believed.

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LASER ENGINEERED NET SHAPING (LENS♦) OF INTERFACES OF FUNCTIONALLY GRADED MATERIALS: *J. E. Smugeresky*[1]; D. M. Keicher[2]; J. A. Romero[3]; M. L. Griffith[3]; [1]Sandia National Laboratories, Livermore, CA 94551 USA; [2]Optomec Design Company, Albuquerque, NM 87185 USA; [3]Sandia National Laboratories, Albuquerque, NM 87185 USA

This paper describes recent developments in LENS® (Laser Engineered Net Shaping) technology, to design the interfaces of functionally graded materials in order to provide electrical isolation in components built directly from CAD solid models. The current LENS® process uses a moving laser beam to fuse solid material particles together by creating a small liquid puddle on a substrate. The solid particles are then injected into this puddle where they dissolve, increasing the volume of the puddle to create the deposited layer by resolidification as the laser beam is moved away. For electrical isolation, depositing liquid particles onto a solid surface may be required. In this work, we examine the mixing of two materials and identify the processing conditions that allow an abrupt material transition to occur at the interface without first melting the substrate. A simple model was developed to predict conditions for melting the particles as they are propelled through the high power laser beam. Statistically designed experiments were used to identify the key process variables critical for achieving good material properties and an abrupt interface transition. The bend tests, optical and transmission electron microscopy for microstructure evaluation, and composition profiles used to assess the integrity of the bonded interfaces are discussed. These results are compared to conventional LENS® processed homogeneous materials. Work supported by the U. S. Department of Energy under contract DE-AC04-94AL85000, and Ballistic Missile Defense Organization SBIR under contract DASG60-97-M-0107

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SLIP CASTING OF RAPID INJECTION MOULDING TOOLS: *Christopher Charles Ainsley*[1]; [1]Nanyang Technological University, School of Mechanical & Production Engineering, Nanyang Avenue, Singapore 639798

This paper discusses how the slip casting process can be used as a forming process for injection moulding tools. Descriptions of the process and the effects of the slip casting parameters on the final casts are given with particular reference to the dimensional tolerances of the final castings. The results show that the slip casting process is suitable for the formation of small injection moulding tools with a 0.12% dimensional tolerance and low distortion. Also shown is the effect casting rate has on the shrinkage of the green parts as well as surface finish. Finally a discussion of the possible befits the slip casting process has over other tooling methods is given.

3:00 PM INVITED PAPER

ORIENTED SHORT FIBER COMPOSITES BY EXTRUSION FREEFORM FABRICATION: Paul Calvert[1]; *Jiong Peng*[1]; [1]AML, 4715 E. Fort Lowell Rd., Tucson, AZ 85712 USA

Extrusion freeform fabrication can be used to build parts from epoxy resins. The resin is blended with a hydrophobic fumed silica to give it the rheology of toothpaste. The part is built and subsequently cured. The same approach can be used to form composite materials with carbon or glass fibers up to about 1mm in length. Moduli up to 3 times that of the base resin can be obtained at a fiber volume fraction of 20%. During the forming process the fibers become closely oriented with the direction of motion of the write-head. This allows fiber orientation to be varied local within the part. Elastic modulus and strength have been measured and are very dependent on the angle between the fiber direction and stress direction. The use of mixed reinforcing fillers to maximize modulus and the combination of soft and tough layers to improve strength will also be discussed.

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COMPLEX STRUCTURAL COMPOSITES FOR BIOMEDICAL APPLICATIONS: *Robert Sinclair Crockett*[1]; Lisa Milkowski[1]; Vito Gervasi[1]; [1]Milwaukee School of Engineering, Rapid Prototyping Center, 1025 N. Broadway, Milwaukee, WI 53202 USA

Solid Freeform Fabrication techniques have been used to produce extremely complex composites that are well-suited for replicating the non-homogeneous mechanical properties of bone. The process begins with Stereolithography patterns consisting of open cellular structures inside a surface shell. Geometry for major structures (e.g. outside shape and regions of various bone densities) are obtained from CT or MRI medical images. Composites are created by using the SFF pattern as a host for filler materials; regions within a single object may be separated by thin barriers, allowing filling with different matrix materials to create regions of differing local properties. The internal structure can also be continually gradiated in thickness to produce composites with properties ranging from that of the filler material to that of the Stereolithography epoxy. Current fillers include epoxy matricies loaded with glass microspheres, as well as hydraulically-bonded ceramic mixtures with bulk properties matched to various bone structures. Results of initial experiments on composites with both discrete and continually gradient properties are presented.

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DIRECT LASER FABRICATION OF HIGH PERFORMANCE METAL COMPONENTS VIA SLS/HIP: *Suman Das*[1]; Joseph J. Beaman[1]; Martin Wohlert[1]; David L. Bourell[1]; [1]University of Texas at Austin, Laboratory for Freeform Fabrication, Mechanical Engineering Dept., ETC 5.160 C2200, Austin, TX 78712-1063 USA

This paper focuses on recent advances in direct freeform fabrication of high performance metal components via selective laser sintering (SLS). The application, known as SLS/HIP, is a low cost manufacturing technique that combines the strengths of selective laser sintering and hot isostatic pressing (HIP) to rapidly produce low volume or "one of a kind" high performance metal components. Direct selective laser sintering is a rapid manufacturing technique that can produce high density metal parts of complex geometry with an integral, gas impermeable skin. These parts can then be directly post-processed by containerless HIP. The advantages of in-situ encapsulation include elimination of a secondary canning step and container material, no container-powder interaction, reduced pre-processing time, a short HIP cycle and reduction in post-processing steps compared to HIP of canned parts. SLS/HIP is currently being developed for INCONEL 625 superalloy and Ti-6Al-4V under a DARPA/ONR program. Microstructure and m echanical properties of material processed by SLS/HIP are comparable to conventionally processed material. The potential of SLS/HIP technology has been demonstrated by fabricating a Titanium guidance section housing for the AIM-9 Sidewinder missile.

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DIRECT LASER FABRICATION OF NICKEL SUPERALLOY CERMET TURBINE ENGINE COMPONENTS: *Suman Das*[1]; Timothy P. Fuesting[2]; Joseph J. Beaman[1]; David L. Bourell[1]; [1]University of Texas at Austin, Laboratory for Freeform Fabrication, Mechanical Engineering Dept., ETC 5.160 C2200, Austin, TX 78712-1063 USA; [2]Allison Engine Company, 2001 South Tibbs, Speed Code W08, Indianapolis, IN 46241 USA

This paper presents the development of a new technique for the production of cermet abrasive turbine blade tips by direct laser processing. These components form part of the low pressure turbine sealing system in an IHPTET demonstrator engine being developed at Allison Engine Company. The influence of laser processing parameters on resulting solidification microstructure and mechanical properties will be presented. Direct laser fabrication of a prototype lot of 100 blade tips was completed successfully. The direct laser fabrication technique results in superior performance and 67% cost reduction over the currently employed production technique. This is the first instance of a direct SFF method applied to the production of functional engine hardware. The next stage of this research is focusing on directly laser fabricating abrasive blade tips onto turbine blades.

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UNDERSTANDING THERMAL BEHAVIOR IN LENS PROCESSING OF STRUCTURAL MATERIALS: *Michelle Griffith*[1]; Lane Harwell[1]; M. Eric Schlienger[1]; John Smugeresky[2]; William Hofmeister[3]; [1]Sandia National Labs, P.O. Box 5800, MS 0958, Albuquerque, NM 87185 USA; [2]Sandia National Labs, P.O. Box 969, Livermore, CA 94551

USA; [3]Vanderbilt University, Dept. of Chemical Engineering, P.O. Box 1604 Station B, Nashville, TN 37235 USA

In direct laser metal deposition technologies, such as the LENS process, it is important to understand and control the thermal behavior during fabrication. Without control of the thermal behavior, components cannot be reliably fabricated with sound material properties. This talk will describe the use of contact and imaging techniques to monitor the thermal signature and history during LENS processing. Recent results show a direct correlation between thermal history and resulting material properties. Microstructural evolution, mechanical properties, and residual stress results will be shown. Development of an understanding of solidification behavior, residual stress, and microstructural evolution with respect to thermal behavior through modeling will be discussed.

SYNTHESIS OF LIGHTWEIGHT METALS III: Aluminum

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. G. McCormick, University of Western Australia, Res. Ctr for Adv. Min. & Mats. Proc., Nedlands, W.A. 6907 Australia

Wednesday PM Room: 10
March 3, 1999 Location: Convention Center

Session Chairs: M. Amateau, Penn State University, Applied Research Laboratory, State College, PA 16804-0030 USA; E.G. Baburaj, University of Idaho, IMAP, Moscow, ID 83844-3026 USA

2:00 PM INVITED PAPER

OVERVIEW OF ALUMINUM - PART I: *John Liu*[1]; F.H. (Sam) Froes[2]; [1]Aluminum Company of America, Alcoa Technical Center, 100 Technical Dr., Alcoa Center, PA 15069-0001 USA; [2]University of Idaho, IMAP, Mines Bldg., Rm. 321, Moscow, ID 83844-3026 USA

The current status of aluminum science, technology and applications will be discussed. This will cover both modifications which have been made to conventional ingot alloys and the development of new families of ingot alloys. It will also include production of aluminum based materials by nonconventional techniques such as Rapid Solidification, Mechanical Alloying and Vapor Deposition. Consideration will also be given to composite concepts including particulate, fiber and lamellae reinforcements.

2:20 PM INVITED PAPER

OVERVIEW OF ALUMINUM - PART II: *John Liu*[1]; F. H. (Sam) Froes[2]; [1]Aluminum Company of America, Alcoa Technical Center, 100 Technical Dr., Alcoa Center, PA 15069-0001 USA; [2]University of Idaho, IMAP, Mines Bldg., Rm. 321, Moscow, ID 83844-3026 USA

The current status of aluminum science, technology and applications will be discussed. This will cover both modifications which have been made to conventional ingot alloys and the development of new families of ingot alloys. It will also include production of aluminum based materials by nonconventional techniques such as Rapid Solidification, Mechanical Alloying and Vapor Deposition. Consideration will also be given to composite concepts including particulate, fiber and lamellae reinforcements.

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SPRAY METAL PROCESSING OF Al-Ce-Co-Cr ALLOYS: *Maurice F. Amateau*[1]; Timothy J. Eden[1]; Michael J. Kaufman[2]; Jay M. Galbraith[1]; Eric J. Fodran[1]; Raymond S. Baker[1]; [1]The Pennsylvania State University, Applied Research Laboratory, Mats. Sci. Division, P.O. Box 30, State College, PA 16804-0030 USA; [2]University of Florida, Dept. of Mats. Sci. and Eng., 132 Rhines Hall, P.O. Box 116400, Gainesville, FL 32611-6400 USA

Al-Ce-Cr-Co alloys processed by rapid solidification rate (RSR) methods exhibit great potential for high strength and high temperature applications. In this work the processing of these alloys by spray metal deposition was investigated to determine if microstructure and mechanical properties similar to RSR processing could be achieved. The effect of processing variables including superheat temperature, gas-to-metal ratio and second particle injection on the resulting microstructure and properties were examined. Processing variables were found to have a pronounce influence on droplet size, dispersoid size, composition and volume fraction. Strength properties to 315ϒC were determined and discussed in terms of microstructure and phase characteristics.

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A NEW APPROACH IN HARDENING OF Al-Fe ALLOYS: *O. N. Senkov*[1]; F. H. (Sam) Froes[1]; V. Stolyarov[2]; R. Z. Valiev[2]; M.D.S. Pirzada[1]; J. Liu[3]; [1]University of Idaho, IMAP, Mines Bldg., Rm. 321, Moscow, ID 83844-3026 USA; [2]Ufa State Aviation Technical University, Institute of Physics and Advanced Materials, K. Marks 12, Ufa, 450000 Russia; [3]Aluminum Company of America, ALCOA Technical Center, 100 Technical Drive, Alcoa Center, PA 15069-0001 USA

Aluminum-iron alloys are attractive for engine application. Unfortunately, the equilibrium solubility of iron in the aluminum lattice is very low even at high temperatures, and these alloys cannot be dispersion-strengthened with the use of conventional thermal treatments. In the present work, the severe plastic deformation approach has been used to extend the iron solubility in a submicrocrystalline aluminum matrix. This allowed aging of the aluminum-iron alloys (5 to 16 wt.% Fe), which resulted in a very high hardness and strength. The effect of aging time and temperature on microhardness of the alloys was also studied.

3:20 PM BREAK

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EFFECT OF MODIFIERS ON THE AS CAST MICROSTRUCTURE OF A390: *E. G. Baburaj*[1]; Jeff Hill[2]; Robert Osborne[2]; *F. H. (Sam) Froes*[1]; [1]University of Idaho, IMAP, Mines Bldg., Rm., 321, Moscow, ID 83844-3026 USA; [2]LA Aluminum Casting, W. 1905 Miles Avenue, P.O. Box 250, Hayden Lake, ID 83835 USA

The hyper-eutectic alloy A390 (Al-17.5Si-0.5Fe-4.5Cu-0.1Mn-0.5Mg-0.1Zn) is the potential choice material for casting automobile cylinders because of its good fluidity, solidification range, strength, rigidity, thermal conductivity, abrasion, wear, and high temperature corrosion resistance along with low thermal expansion coefficient. The extensive use of this alloy is limited by its low ductility. The present work is an attempt to improve the ductility through the control of microstructural features of A390 by the addition of trace elements.

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SECONDARY PHASE SELECTION IN 1XXX ALUMINUM ALLOYS: AN OVERVIEW: *C. M. Allen*[1]; K. A. Q. O' Reilly[1]; B. Cantor[1]; P. V. Evans[2]; [1]University of Oxford, Dept. of Mats., Oxford Centre for Advanced Materials and Composites, Parks Rd., Oxford OX1 3 PH UK; [2]Alcan International, Ltd., Banbury Laboratory, Southam Rd., Banbury, Oxon OX16 7SP UK

1xxx series Al alloys are used in a wide variety of wrought applications, including packaging foil, anodised sheet for architectural use and lithographic printing sheet. These products are commonly direct chill (DC) cast to form ingots, which are then heat treated and rolled to the required final gauge. Alloying additions and impurities together constitute typically <1wt% of the alloy composition. Consequently the as-solidified microstructure contains only ~1vol% of secondary phases, in the form of Fe and Si based aluminides. These aluminides however influence material properties such as strength, resistance to fracture, ductility and surface electrochemistry, which in turn affect downstream

processing requirements and final bulk and surface properties. Model 1xxx Al alloys have been rapidly solidified to produce a dispersion of submicron phases entrained in an Al matrix. On heating these phases melt eutectically to produce a highly dispersed liquid in a solid Al matrix. On subsequent cooling therefore the nucleation requirements for solidification are much exaggerated. The solidification of the dispersed liquid can be studied calorimetrically, which provide valuable information on the change of phase content with changes in alloy trace chemistry and solidification rate. The dispersion technique has shown that <100ppm of V impurity in combination with Al-Ti-B grain refiner addition promotes the formation of a metastable phase, responsible for the well know 'fir-tree' surface defect in DC castings. This unequivocally demonstrates that certain impurities and grain refiners have a potentially strong influence on the nucleation aspects of secondary phase selection during conventional solidification, which until now have largely been overlooked or poorly understood.

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NANOCRYSTALLINE Al-Ni-Y ALLOYS: *M. Gogebakan*[1]; P.J.S. Warren[1]; B. Cantor[1]; [1]University of Oxford, Dept. of Mats., Oxford Centre for Advanced Materials & Composites, Parks Road, Oxford OX1 3PH UK

This paper describes the manufacture of amorphous and nanocrystalline Al-Ni-Y alloys by a combination of melt spinning and heat treatment. The effects of alloy composition and quenching rate are discussed in detail. The crystallisation process has been investigated by a combination of differential scanning calorimetry, transmission electron microscopy, X-ray diffractometry and kinetic analysis.