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

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

Thursday AM Room: 15B
March 4, 1999 Location: Convention Center

Session Chair: Michael Wargo, NASA Headquarders, Washington, DC USA

8:30 AM
OVERVIEW OF ALTERNATE CONTAINERLESS TECHNIQUES: *Rick Weber*[1]; [1]Containerless Research, Inc., 906 University Place, Evanston, IL 60201-3149 USA

Containerless processing methods provide a high-purity environment to study high-temperature materials and non-equilibrium states of matter. This talk will identify and review containerless processing techniques which are based on technologies not represented by ELF, TEMPUS, or Space-DRUMS. The technology issues and research capabilities associated with each will be assessed.

8:50 AM
OPTICAL DIAGNOSTIC TOOLS: *Shankar Krishnan*[1]; [1]Containerless Research, Inc., 906 University Place, Evanston, IL 60201-3149 USA

Optical diagnostic tools represent a key technology required for containerless processing. Optical pyrometry provides temperature measurement. Optical position sensing devices are required for controlling specimen location during processing. High-performance cameras provide data for thermophysical property measurement.

9:10 AM
LESSONS LEARNED FROM CONTAINERLESS PROCESSING FACILITIES: *Jan Rogers*[1]; [1]NASA Marshall Space Flight Center, Mail Code ES76, MSFC, AL USA

Containerless processing experiments have been performed in several reduced gravity settings and in ground-based laboratories. Lessons learned from acoustic, electromagnetic, and electrostatic levitation devices are valuable for future containerless research. There will be a panel discussion on this topic.

9:30 AM
DEFINITION OF TARGETS FOR SCIENTIFIC RESEARCH USING LEVITATION TECHNIQUES: *Michael Wargo*[1]; [1]NASA Headquarters, Code UG, Washington, DC 20546 USA

Targets identified will include materials of interest, scientific data which can be obtained, and technical requirements for levitation. There will be a panel discussion on this topic.

9:50 AM BREAK

10:10 AM
DEFINITION OF SPECIFIC EXPERIMENT TYPES FOR EACH ISS LEVITATION FACILITY: *Shinichi Yoda*[1]; [1]NASDA, Space Utilization Research Center, Sengen, 2-1-1, Tsukuba-shi, Ibaraki-ken 305 Japan

Each levitation facility will provide unique environments for performing containerless research. An attempt will be made to categorize experiments which are best performed in each of the planned facilities. There will be a panel discussion on this topic.

10:40 AM
IDENTIFICATION OF DIAGNOSTIC TOOLS FOR ISS CONTAINERLESS RESEARCH AND COMMON REQUIREMENTS: *Rainer Kuhl*[1]; [1]DLR, Koenigswinterer4, Str. 522-52, Bonn 53227 Germany

To take advantage of the full capabilities of containerless facilities, a number of diagnostic tools must be developed and added. A discussion of the existing and desired diagnostic techniques will be included. There will be a panel discussion on this topic.

11:10 AM
RECOMMENDATIONS FOR FACILITY MODIFICATIONS TO ENHANCE SCIENCE: *Philip Gregory*[1]; [1]Canadian Space Agency, 6767 Route de l'Aeroport, St-Huber, Quebec J3Y 8Y9 Canada

Facility modifications may be necessary to accomplish on-going research in the planned containerless facilities. A discussion of the compatibility and desired modifications will be included. There will be a panel discussion on this topic.

11:40 AM
IDENTIFICATION OF LEVEL OF INTEREST IN SPECIFIC TECHNIQUES OR EXPERIMENT TYPES: *Ivan Egry*[1]; [1]DLR, WB-RS, Institut fuer Raumsimulation, Cologne, 0551140 Germany

Since the planned containerless facilities will service a wide ranging international community, a discussion of the level of interest for each facility as appropriate to each research group will be included. There will be a panel discussion on this topic.

ALUMINUM REDUCTION TECHNOLOGY: Fundamental Studies

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

Thursday AM Room: 6F
March 4, 1999 Location: Convention Center

Session Chair: Jean-Paul Huni, Alcan International, Ltd., Arvida Research & Development Centre, Jonquiere, Quebec G7S 4K8 Canada

8:30 AM
A TWO ELECTRON PROCESS PRODUCING CO AND A FOUR ELECTRON PROCESS PRODUCING CO_2 DURING ALUMINIUM ELECTROLYSIS: *T. S. Sorensen*[1]; S. Kjelstrup[2]; [1]DTH, Physical Chemistry, Modeling and Thermodynamics, Norager Plads 3/DTH, Copenhagen-Vanlose, Sjaelland DK2720 Denmark; [2]NTNU, Physical Chemistry, S. Saelands vei 14, Trondheim, Troendelag N-7034 Norway

Earlier measurements of anode potentials in the Hall-Heroult cell, have been re-analyzed in terms of two parallel Butler-Volmer processes. The RI-corrected electric potential differences between a working car-

bon anode and a non-working Al reference electrode were measured. The current density is found as the sum of Butler-Volmer expressions for a two electron process (producing CO) and a four electron process (producing CO_2). Each process is associated with its own overpotential. We propose that the $Al_2O_2F_4)^{2-}$ ion is responsible for the CO_2 production. This ion forms an activated complex with an O-atom placed on each side of a reactive surface carbon atom. The negative, effective activation energy for the n=4 process is explained by the thermodynamic behaviour of this species in the acid NaF-AlF_3-CaF_2-Al_2O_3 melt. The Pearson-Waddington relation overestimates the percentage of CO_2 by disregarding electrolytically produced CO which dominates at lower potentials (current densities).

8:55 AM

THE KINETICS AND MECHANISM OF THE ELECTRODE REACTIONS IN ALUMINIUM ELECTROLYSIS: *A. Kisza*[1]; J. Kazmierczak[1]; J. Thonstad[2]; T. Eidet[2]; J. Hives[3]; [1]University of Wroclaw, Faculty of Chemistry, 14 Joliot, Curie, Wroclaw 50383 Poland; [2]NTNU, Dept. of Electrochemistry, 7034 Trondhelm Nowway; [3]SUT, Dept. of Inorganic Technology, Bratislava 81237 Slovakia

With the use of electrochemical techniques, the kinetics and mechanism of the cathodic and anodic reactions in aluminium electrolysis was determined at several electrolyte compositions, and in particular in a typical industrial bath, i.e. cryolite with 11 wt% AlF_3, 3 to 5 w% CaF_2 and variable alumina concentrations at 1000℃. A three step electrode process was observed for the cathodic reaction, comprising a preceeding chemical reaction followed by two charge transfer steps. The exchange current density of the cathodic reaction was found to be dependent upon the concentration of the aluminium fluoride ionic species. Also the anodic reaction was found to proceed according to a three step mechanism involving a preceding chemical reaction and two charge transfer steps with intermediate adsorption. The experimental data gave the double layer capacitance, electrode coverage, effective rate constants, the charge needed for the coverage of the electrode by a monolayer and coefficients of the Tafel equation. The role of the two additives, AlF_3 andCaF_2 was evaluated.

9:20 AM

VISCOSITY OF OXYFLUORIDE MELTS RELATED TO THE DETERIORATION OF REFRACTORY LININGS IN ALUMINUM REDUCTION CELLS: *T. Grande*[1]; J. Rutlin[1]; [1]Norwegian University of Science and Technology, Inorganic Chemistry, Trondheim N-7034 Norway

Molten fluoride attack on refractory pot linings increases the energy consumption and may in extreme cases terminate the pot life. The diffusion of molten fluorides down into refractory pot linings is determined by the viscosity of the melt which penetrates/reacts with the refractory lining. In the present paper estimated viscosities of molten mixtures of fluorides and sodium aluminum silicates are reported. The viscosity is estimated by use of a semi-empirical theory which relates viscosity to heat capacity of melts in the glass transition region. The viscosity of the fluorides is increasing several orders of magnitude when albite and nepheline are dissolved in molten fluorides. The present findings demonstrate that the penetration of molten fluorides into traditional fireclay refractories is strongly retarded due to the formation of a viscous oxyfluoride layer between the cathode and the refractory lining. Finally, the formation of the viscous layer is discussed in terms of the silica-content in the refractory lining.

9:45 AM

LABORATORY CHARACTERIZATION OF THE INTERACTIONS BETWEEN CRYOLITIC BATHS AND REFRACTORIES: *G. Oprea*[1]; [1]University of British Columbia, Metals and Materials Engineering, 309-6350 Stores Rd., Vancouver, BC V6T 1Z4 Canada

Refractories in the SiO_2 - Al_2O_3 system were investigated using a testing method with six different preparation procedures for bricks, mortars and dry-barrier powders and various testing conditions. The corrosion results were correlated with chemical and mineralogical compositions, at the refractory - melt interface, for couples refractory - bath, ranging from 20 to 50% Al_2O_3 for refractories and 1.2 to 2.5 bath ratio by weight for the cryolitic bath. A "corrosion criterion" was defined based on individual corrosion parameters and used in evaluating the performance of a refractory material in contact with molten cryolitic baths.

10:10 AM BREAK

10:30 AM

ACTIVITY OF ALUMINA IN THE SYSTEM NAF - AlF_3 - Al_2O_3 AT NaF/AlF_3 MOLAR RATIOS RANGING FROM 1.4 TO 3: *A. Solheim*[1]; Å. Sterten[2]; [1]SINTEF, Materials Technology, Trondheim N-7034 Norway; [2]Norwegian University of Science and Technology, Dept. of Electrochemistry, Trondheim N-7034 Norway

The activities in the ternary liquid system NaF - AlF_3 - Al_2O_3 were derived. The results are presented in the form of two sets of empirical equations; one set describing the activity of each component at 1300 K as a function of the melt composition, and the other set describing the temperature dependence of the activities. The derivation was based on mathematical functions attributed to each component, those functions being consistent with the Gibbs-Duhem equation. By varying the constants in the functions, finally good agreement was obtained with experimental data available in the literature, such as heat of dissolution, liquidus temperature, alumina solubility, vapour pressure, and emf of electrochemical concentration cells.

10:55 AM

LOWERING THE ANODIC OVERVOLTAGE BY DOPING THE CARBON ANODES IN ALUMINIUM ELECTROLYSIS: *J. Yang*[1]; Q. Zhang[1]; J. Thonstad[2]; Y. Liu[1]; [1]Central South University of Technology, Dept. of Metallurgy, Changsha, Hunan Province 410083 China; [2]Norwegian University of Science and Technology, Dept. of Electrochemistry, Trondheim N-7034 Norway

A laboratory study has shown that the anodic overvoltage in aluminium electrolysis can be lowered by adding doping agents to the carbon anodes. For anodes doped with 1 wt.% AlF3 or 0.5 wt.% MgAl2O4, the anodic overvoltage at 0.8 A/cm2 decreased by 50-70 mV compared with undoped anodes, in a melt with Na3AlF6 - 11 wt% AlF3 - 5 wt% CaF2 - Al2O3 (sat.) at 970°C. An improved current interruption technique and a special cell configuration were used. A substantial increase in anodic overvoltage was observed by bubbling CO through the melt. The air and CO2 reactivities of the doped anodes were markedly lower than that of identical undoped anodes.

11:20 AM

ACTIVITIES IN THE SYSTEM KF-AlF_3: *Ø. T Gustavsen*[1]; Terje Østvold[1]; [1]NTNU, Dept. of Inorganic Chemistry, Sem Sælandsv. 12, Trondheim, 7034 Norway

Activities in the system KF-AlF_3 have been measured. In the acidic melts (CR<3) activities of $KAlF_4$ were calculated from vapour pressures and vapour composition data. In the basic part of the diagram (CR>3), the vapour pressures are, however, too low to give accurate pressure data. For this range a model which give vapour pressures of $KAlF_4$ from composition data of the vapour over the melts and the standard vapour pressure of KF has been developed. Activities in the basic region can be obtained from these calculated pressures. The activities of KF are obtained from the activities of $KAlF_4$ using the Gibbs-Duhem equation. Thereafter, mole fraction based activity coefficients of $KAlF_4$ and KF are calculated as gamma(i)=a(i)/x(i) , where x(i) are the real mole fractions as obtained by Raman spectroscopy.

11:40 AM

DISSOLUTION OF ALUMINA IN CRYOLITE BATH: *Z. Qiu*[1]; Z. Yang[1]; Z. Wang[1]; W. Li[1]; B. Kao[1]; X. Sun[1]; [1]Northeastern University, Dept. of Non-ferrous Metallurgy, Shenyand 110006 China

In this paper we report our experimental results of alumina dissolution in molten cryolite. The dissolution process was observed in a laboratory see-through cell. The dissolution process consists of several stages: (1) Floating of cold alumina on the surface of molten bath, (2) Disintegration of the floating alumina layer into fine alumina particles and flakes of alumina-cryolite agglomerates, (3) Dissolution of alumina in the bulk of the molten bath during its settling from the floating layer, and at the cell bottom after it settles down there. The dissolution time and behaviour of alumina were recorded with a video camera.

CAST SHOP TECHNOLOGY: Equipment & Handling

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

Thursday AM Room: 6C
March 4, 1999 Location: Convention Center

Session Chair: Edmund Hemmersbach, Commonwealth Aluminum Corp., Lewisport, KY 42351-0480 USA

8:30 AM
THE ANATOMY OF A CAST SHOP PROBLEM SOLUTION: *George J. Binczewski*; [1]SC Systems, P.O. Box 6154, Moraga, CA 99570 USA

Changing environmental concerns together with their inevitable regulations and restrictions often present complex and vexing problems to the cast shop practitioner. Invariably, this requires process and procedural modifications which almost always result in cost increases. By referencing a series of seemingly unrelated cast shop technological evolvements spanning a period of twenty years, an innovative method was developed. It utilized the application of a common material to solve a serious concern. Importantly, the material exhibits characteristics which offer significant potential for other cast shop operations.

8:55 AM
MOLTEN METAL CONTACT TESTING OF MORTAR JOINTED FURNACE BRICKS: *A. G. Furness*[1]; A. J. Forde[1]; [1]Alteck Limited, 2 Becton Mead, Becton Lane, Barton on Sea, New Milton, Hants BH25 7DL UK

In the aluminium industry it is common knowledge that the conversion of bricked furnace linings to a-AI2O3 is frequently initiated at the mortar joints. The question of how best to assess the behavior of mortar joints in molten aluminium, initiated a review of published techniques for the liquid metal testing of refractories and from these, the method to be utilized was finally selected. That most appropriate to mortar jointed samples was the Immersed Finger Test (IFT), in which individual 25 X 25 X 225mm refractory samples are partially immersed in a 1 kg crucible of the preferred alloy, at a selected temperature for no less than 7 days. Daily metal sampling of each crucible is carried out to determine if any alloy contamination had taken place. A novel method was employed to maintain permanent joints between the bricks/mortar sandwich. This enabled 42%, 80% Al2O3 and an aluminium resistant brick to be tested, at 900°C, each with two different mortars both in A.A 6063, the Worlds largest tonnage alloy and A.A7075, known to be particularly aggressive to refractories. The results demonstrated that in most cases the 42 & 80% Al2O3 bricks suffered significant a-AI2O3 conversion in contact with both alloys, leaving the mortar largely unaffected. The aluminium resistant brick showed minor conversion against 7075. The integrity of brick/mortar joints was maintained during and after all tests, also no significant difference existed in the degree of conversion relative to the 'as made' or cut faces of the test samples.

9:20 AM
OPTIMIZING BURNERS FOR ALUMINUM MELTING AND HOLDING FURNACES WITH ULTRA LOW NO_X DESIGNS: *Frank L. Beichner*[1]; [1]Bloom Engineering Company, Inc., Sales Engineer - Non-Ferrous Products, 5460 Horning Rd., Pittsburgh, PA 15236 USA

Recent EPA restrictions on POC emissions from aluminum melters and holders have necessitated burner designs with extremely low NOx and CO emission levels along with flame patterns to provide optimum melting. Recent breakthroughs in burner technology has led to the development of the recuperative LumiFlameä design that uses two modes of operation based on the furnace operating and melting requirements. This design provides a high intensity low NOx burner design operating mode for melting the initial charge, along with a LumiFlame ultra low NOx mode to be used when raising the molten bath to pour temperature. With this design there is no compromise with furnace performance when extremely low NOx emissions are required.

9:45 AM
VORTEX CHARGE WELL WITH GAS LIFT PUMP AND GRAVITY FURNACE CHARGER: *Larry D. Areaux*[1]; [1]Premelt Pump, Inc., 2205 Miller Road, Kalamazoo, MI 49001 USA

This paper presents the latest technological development in high capacity aluminum scrap melting in a reverberatory furnace with melt yields above 96% when charging aluminum chips, foil or UBC. The process combines submerged charging through a self-leveling Charge Well Cover, a Vortex Charge Well and a nitrogen operated, Gas Lift Molten Metal Circulating Pump. Employed to produce the Vortex stirring action while circulating several thousand pounds of molten aluminum per minute throughout the main chamber of the melt furnace. This development creates an oxygen deprived environment in which aluminum scrap in its lightest fraction can be continuously submerged into a bath of circulating molten metal for rapid conversion into its liquid state. The inert gas being discharged from the Molten Metal Circulating Pump below the Charge Well Cover, provides additional benefits in achieving the exceptionally high metal quality and melt yield.

10:10 AM BREAK

10:30 AM
CONTINUOUS IN-LINE MONITORING OF Mg CONTENT IN ALUMINUM MELTS: *Johan Vangrunderbeek*[1]; Pieter Lens[1]; Paul Verstreken[2]; Cees Castelijns[3]; [1]VITO, Process Technology, Boeretang 200, Mol B-2400 Belgium; [2]Heraeus Electro-Nite Int. NV, R&D, Centrum Zuid 1105 B1, Houtalen B-3530 Belgium; [3]Hoogovens Aluminium NV, Quality Dept., A. Stocletlaan 87, Duffel B-2570 Belgium

Magnesium is an important alloy addition to aluminum for can stock and automotive components in particular. The successful development of magnesium sensors for aluminum alloys has made continuous real-time and in-line measurement of magnesium content in the cast possible. Plant evaluation indicated that the sensor possessed sufficient accuracy and stability for process monitoring and control. The working mechanism of the magnesium sensor is briefly described and the results of sensor applications in laboratory experiments as well as in plant trials are presented.

10:55 AM
MINIMIZING METAL LOSS AND ENERGY DURING MELTING AND HANDLING OF MOLTEN ALUMINIUM AND UTILIZATION OF VALUABLE DROSS TO SAVE A FORTUNE: *Wolfram S. Ruff*[1]; [1]Consultant, 21680 Stade, Hempbarge Germany

Millions of tons of Aluminium are produced every year and a certain percentage of this amount is lost by conversion to Alumina during process. To minimise metal loss and amount of dross, one has to take care about the mechanism of oxidation during every step of operation. Oxidation depends on five parameters which are affecting metal loss or vice versa savings, If optimised. From scrap or tapped metal, during charging, melting, alloying, metal treatment, skimming down to casting, all parameters are discussed and improvements are shown. But even with the very best technology there will be dross, which has to be cooled immediately after skimming and processed to get as much valuable metal back as possible. My Credo for total metal handling and secondary dross processing: Use the best available technology, with minimum metal loss, smallest amount of residues, most economic treatment of said residues and then YOU ARE ABLE TO SAVE A FORTUNE!

CAST SHOP TECHNOLOGY: Molten Metal Processing/Filtration

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

Thursday AM Room: 6D
March 4, 1999 Location: Convention Center

Session Chair: C. William McCormick, McCormick & Associates, Sydney, NSW 2075, Australia

8:30 AM

STAGED FILTRATION EVALUATION AT AN AIRCRAFT PLATE AND SHEET MANUFACTURER: *Michael M. Niedzinski*[1]; David D. Smith[1]; Leonard S. Aubrey[2]; [1]McCook Metals, Chief Metallurgist, 1st Ave. & 47th St., McCook, IL 60425 USA; [2]SELEE Corporation, 700 Shepherd St., Hendersonville, NC 29792 USA

SELEE Corporation has recently developed a staged filtration system, utilizing two standard ceramic foam filters (CFF) in series, which improves metal filtration capabilities beyond that of standard single element system, yet retains all the advantages of single element ceramic foam filtration system. Some of the advantages retained include operator acceptance and alloy flexibility. McCook Metals recently evaluated this system on 7XXX series alloys using both LiMCA II and LAIS techniques. Additionally an attempt was made to correlate the LiMCA II results with ultrasonic plate recovery. In addition LiMCA data was obtained on a standard single filter element system and a filter containing a coarse/fine duplex pore size structure. LiMCA results indicated that with the staged filtration system average N20 inclusion contents down to 100 particles per kilogram (0.1 k/kg) were obtainable. These excellent results were followed by other combinations including the duplex filter and then by a standard single ceramic foam filter element. Comments on potential future applications and benefits will be reviewed.

8:55 AM

EVALUATION OF THE EFFICIENCY OF FINE PORE CERAMIC FOAM FILTERS: *Neil J. Keegan*[1]; Wolfgang Schneider[2]; Hans-Peter Krug[2]; [1]Foseco International, Ltd., Aluminium, P.O. Box 5516, Tamworth, Staffs B78 3XQ UK; [2]VAW Aluminium AG, R&D, Georg-v. Boeselager-Strasse 25, Bonn D-53117 Germany

Melt treatment leading to inclusion removal is an important process step in the production of d.c. cast ingots so as to limit defects during the subsequent processing of these ingots into the finished product. A range of in-line treatment methods are available for their removal. Currently the most widely used method is by filtration of the liquid aluminium using a porous media, namely ceramic foam. With the objective of investigating the performance characteristics of a range of in-line filtration systems, in particular that of ceramic foam filters, a joint programme of work has been ongoing between Foseco and VAW - R&D since 1995. The latest phase of this programme has investigated the use of fine and ultrafine pore ceramic foam filters with cell sizes down to 650 microns. This extends the earlier ceramic foam filter trials by investigating CFF's with cell sizes which are closer to the mean pore diameters of the tube filters trialed earlier. Trials under carefully controlled plant conditions were undertaken on 50ppi, 65ppi and 80ppi porosity filters in addition to those of coarser 30ppi CFF's Their performance has been monitored using LiMCA II, PoDFA and LAIS. This paper presents a comparison of the relative performance of these filters and compares these results with those of other in-line filtration systems. It also considers both the physical characterisation of the CFF's and some of its important structural characteristics along with metallographic evaluation of the spent ceramic foam filters themselves.

9:20 AM

RECENT IMPROVEMENTS IN CERAMIC FOAM FILTER BOWL DESIGN BY COUPLED HEAT AND FLUID FLOW MODELLING: *Gerd Ulrich Gruen*[1]; Wolfgang Schneider[1]; Steven F. Ray[2]; Jan-Olaf Marthinusen[2]; [1]VAW Aluminium AG, Research & Development, Georg-von-Boeselager-Strasse 25, Bonn D-53117 Germany; [2]Foseco International, Ltd., P.O. Box 5516, Tamworth, Staffordshire B78 3XQ England

Increasing demands on metal quality and ongoing improvements in the application of ceramic foam filters have secured the use of this technique to treat molten aluminium. It now offers a simple, reliable and cost effective method to remove inclusions from liquid aluminium which is an important part of meeting the quality demands of specific product applications of DC cast aluminium ingots. The importance of metal cleanliness to a modern casthouse led Foseco and VAW to jointly examine the design of current filter bowls. The flow patterns in the bowls were optimised by coupled heat transfer and fluid flow modelling for the initial and stationary phase. The paper demonstrates the design principles used and some of the problems with the traditional bowl designs with particular regard to the flow field in the outlet area. A stepwise approach was used to improve the design. The heat and fluid flow modelling results at each step were calculated and the benefits are reviewed. Finally, the fluid flow in a standard bowl is compared to a fully optimised bowl.

9:45 AM

DEVELOPMENT OF A COMPACT DEEP BED FILTER FOR ALUMINIUM: *Martin Syvertsen*[1]; Frede Frisvold[2]; Thorvald Abel Engh[1]; Didrik S. Voss[3]; [1]Norwegian University of Science and Technology, Dept. of Metall., Alfred Getz vei 2b, Trondheim N-7034 Norway; [2]SINTEF , Mats. Tech., Alfred Getz vei 2b, Trondheim N-7034 Norway; [3]Elkem Aluminium ANS, Lista, Farsund N-4550 Norway

A new deep bed filter has been developed and tested in production runs at Elkem Aluminium ANS, Lista, Norway. The filter is cylindrical and the melt moves axially downwards. It thus has a more compact design and utilises the filter media more efficiently than conventional deep bed filters. Objectives were to investigate the mechanisms of inclusion removal and "ageing" of the deep bed filter. During operation, samples of the melt were taken before and after the filter. Samples were taken both at the start-up, in the middle and towards the end of the test period. The samples were studied metallographically using automatic image analysis. Size distributions of inclusions in and out of the filter were obtained and filtration efficiencies were determined. Removal may be explained in terms of an interception mechanism. When the efficiency dropped only 2% of the void volume was occupied by inclusions.

10:10 AM BREAK

10:30 AM

PRODUCTION SCALE EVALUATION OF NEW DESIGN CERAMIC FOAM FILTER: *Jennifer Black*[1]; Gary Parker[2]; Tabb Williams[2]; [1]Vesuvius Hi-Tech Ceramics, P.O. Box 788, Alfred, NY 14802 USA; [2]Reynolds Metals Company, 13203 N. Enon Church Rd., Chester, VA 23831 USA

The aluminum industry has widely accepted the standard flat surface ceramic foam filter for use in a wide range of product quality requirements. Over the past 20 years, there have been relatively few revolutionary improvements in the basic flat filter design. Vesuvius Hi-tech Ceramics has now developed and patented a high surface area, ceramic foam filter for use in molten aluminum. A cooperative program between Reynolds Metals Corporation R&D and Vesuvius Hi-Tech Ceramics was established to investigate the performance of the Vesuvius "New Wave" high surface area filter versus their commonly used, flat ceramic foam filter. The objective of the program was to compare the Vesuvius "New Wave" filter to their standard flat ceramic foam filter under actual production conditions. Production scale casting of DC 5182 ingot was conducted at the Reynolds Corporate R&D Casthouse. The flow rate per unit area of filter was made comparable to typical DC production facilities. The two filter types, standard and "New Wave", were evaluated as 40 ppi and 50 ppi filters producing four filter categories. A total of 12 casts were made to evaluate the four filter categories. Filtration efficiencies using LiMCAII results will be presented, along with LAIS results and operational differences for the flat and "New Wave" filters.

10:55 AM

MODELING OF GROWTH AND SEPARATION OF INCLUSIONS IN METALS REFINING SYSTEMS: *Nagy El-Kaddah*[1]; David Godard[2]; Pierre-Yves Menet[3]; [1]The University of Alabama, Dept. of Metall. Eng., P.O. Box 870202, Tuscaloosa, AL 35487 USA; [2]Pechiney CRV, PB 27, Voreppe 38340 France; [3]Pechiney Rhenalu, Z.I. Biesheim, B.P. 49, Neuf-Brisach F-68600 France

Theoretical models of inclusion removal in aluminum melt treatment systems need to account for effects of flow and turbulence on transport, coalescence and separation of dispersed phases. Traditional models based on discrete particle flow or continuum species transport ignore some of these effects. This paper presents a population balance model for describing the dynamic behavior and separation inclusion particles in a stirred molten metal. It is based on the solution of a modified Smoluchowski population balance equation that allows for convective transport of inclusions in the melt. The procedure for solving coupled fluid flow and particle balance equations is also described. The model was tested by comparing model predictions against measured rates of removal of 10 mm SiC and Al2O3 particles in levitated aluminum droplets. The excellent agreement obtained between measurements and predictions regarding both the evolution of particle size distributions and the rate of inclusion removal shows a full validation of the technique employed.

11:20 AM

THE MEASUREMENT OF CONTROLLED SIZE PARTICLES IN MOLTEN ALUMINUM USING THE LIMCA TECHNIQUE: *C. Dupuis*[1]; [1]Alcan International, Ltd., Arvida Research and Development Center, Jonquiere, Quebec Canada

The LiMCA technique allows the measurement of nonmetallic particles suspended in molten aluminium based upon the resistive pulse principle. The size of the particles measured is based on their volume and is reported as the diameter of the equivalent sphere. In order to verify the calibration of the LiMCA, metal samples containing controlled size particles were prepared and analyzed using LiMCA. This paper presents the results obtained with the LiMCA in comparison with the measurements done by other techniques. It will be shown that for regular shape inclusions, the size distribution obtained from the LiMCA is in good agreement with the one obtained by other characterization methods. The effect of sample preparation and particle shape will also be discussed.

FLUID-FLOW PHENOMENA IN METALS PROCESSING: Metals Refining and Aqueous Processing

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, 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

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

Session Chairs: Knut Halvard Bech, SINTEF, Materials Technology, Trondheim, N-7034 Norway; Ramana Reddy, The University of Alabama, Dept. of Metall. and Mats. Eng., Tuscaloosa, AL 35487-0202 USA

8:30 AM

MAGNETIC FIELD CONTROL OF THE MELT EXTRACTION PROCESS: A. Cramer[1]; *Gunter Gerbeth*[1]; [1]Research Center Rossendorf, Inc., P.O. Box 510119, Dresden D-01314 Germany

The production of highly porous metallic substrates requires an effective and well-controlled production of metallic fibres with diameters in the range of 20 to 200 microns. The liquid melt extraction, where a quickly rotating wheel extracts the fibres directly out of the inductively heated melt, is a promising technology for that purpose. Up to now instabilities caused by the rotating wheel and the temperature gradients in the melt did not allow a reproducable production of controlled fibre diameters. The idea is to suppress these instabilities by suitable external magnetic fields. We present model experiments on the influence of steady magnetic fields on the melt surface instabilities, the meniscus at the boundry between wheel and melt, and the diameter distribution of the finally produced fibres. The model experiments are performed with an eutectic tin-lead alloy. Real-scale results for NiAl and other high-temperature melts will also be given. The magnetic field has a serious stabilizing influence on the process.

8:50 AM

FLOW INSTABILITIES IN VAR: *P. A. Davidson*[1]; [1]University of Cambridge, Eng. Dept., Trumpington St., Cambridge CB2 1PZ UK

We discuss a well-known but much misunderstood instability which occurs in Vacuum Arc Remelting. In the absence of buoyancy, the dominant force on the pool arises from the interaction of the current flow and its self magnetic field. The resulting flow is poloidal. However, it is well known that very small, stray magnetic fields can induce an intense swirling motion. This is usually attributed to the breakdown of a self-similar solution for the poloidal flow. We show that this is not the case, and that the true explanation lies in the action of the Ekman pumping.

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CONVECTIVE HEAT TRANSFER DURING ELECTRON BEAM EVAPORATION OF LIQUID METALS: *Christian Karcher*[1]; R. Schaller[1]; A. Thess[1]; [1]Dresden University of Technology, Institute for Aerospace Engineering, Center for Physical Fluid Mechanics, Dresden D-01062 Germany

Electron beam evaporation of liquid metals is an innovative technology increasingly used in industry to produce very thin coatings of high purity. In this process the surface of a metal ingot, placed in a water-cooled copper crucible, is heated by bombarding it with a high-energy electron beam gun. The material melts, forming a free surface and eventually starting to evaporize. The rising vapor cloud condensates as thin film on a moving substrate. The strong energy input at the free surface gives rise to vigorous thermocapillary and buoyancy-driven convective motion within the melt leading to unwelcome heat losses. The present paper aims to show how these losses can be reduced by optimizing the geometry of the cruicible and by using external magnetic fields. We present both experimental and numerical results.

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OXYGEN-ENRICHMENT OF SIDE-WELL ALUMINUM FURNACES: *Charles E. Baukal*[1]; [1]Air Products and Chemicals, Inc., Global Applications Development, 7201 Hamilton Blvd., Allentown, PA 18195 USA

Reverberatory furnaces play a significant role in the aluminum melting industry. Optimizing the heat and mass transfer in these furnaces reduces the capital, operating, and maintenance costs. The use of oxygen-enriched air/fuel firing or pure oxy/fuel firing can reduce the melting cycle, fuel consumption, and total emissions from the furnace. Control of the oxygen content at the aluminum surface is also important for reducing metal losses which means increased yields. Improper use of oxygen-enriched or pure oxygen firing technology in aluminum reverb furnaces as practiced in the past has resulted in furnace damage and metal loss from local overheating. Many questions remain to be answered about new oxy/fuel technologies. Aluminum producers need to be convinced of the benefits of new technology involving oxygen enhanced combustion. To answer many of the questions and to try to optimize the heat and mass transfer in aluminum reverb furnaces, a 3-D computer model was developed which couples the combustion space and the molten aluminum bath. Prior models considered only the combustion space. This new model solves the mass and the energy transfer equations in both media simultaneously. Turbulent flow in the combustion space interacts with viscous laminar flow in the melt. Conduction, convection and radiation heat transfer mechanisms are included in the model. Improved understanding of the furnace operation is based on temperature, velocity, and species concentration in the combustion space and the molten bath. Typical results are presented for an aluminum side-well furnace with air/, air-oxy/, and oxy/fuel combustion systems. It will be shown that oxygen-enriched combustion has a significant advantage over air/fuel systems. A properly designed oxy/fuel system can increase furnace production and fuel savings while minimizing pollution emissions. The newly-developed model is a powerful tool for process and geometry optimization in aluminum reverb furnaces.

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VISCOSITY MEASUREMENT AND MODELING OF BORATE AND BOROSILICATE MELTS: *Zhijing Zhang*[1]; Ramana G. Reddy[1]; [1]The University of Alabama, Dept. of Metall. and Mats. Eng., A129 Bevill Bldg., 126 Seventh Ave., P.O. Box 35487-0202, Tuscaloosa, AL 35487-0202 USA

The viscosity of molten oxides is one of the important physical properties since viscosity has a decisive influence on fluid flow. The knowledge of the viscosity of molten oxides is essential for modeling and controlling of metallurgical process. In the present study, viscosities of Na2O-SiO2-B2O3 ternary melts were measured as a function of temperature and composition. Experiments were carried out using rotary viscometer and graphite components. Our experimental results were compared with those in literature. Based on the current experimental data, the previously developed viscosity model was modified. The characteristic features of viscosities of these melts have been discussed. The predicted viscosity results are in excellent agreement with the present experimental data in the temperature range with molten state samples.

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MATHEMATICAL MODELING OF THE FLUID FLOW FIELD IN AN ELECTROLYSIS CELL: *Andreas Filzwieser*[1]; Klaus Hein[1]; Peter Paschen[1]; Herwig Grogger[2]; [1]University of Leoben, Dept. of Nonferrous Metall., Franz-Josef-Straße 18, Leoben A-8700 Austria; [2]AVL LIST GmbH, Hans-List-Platz 1, Graz, Styria A-8020 Austria

The fluid flow in a copper refining cell is calculated with a closer look to the mass transport phenomena in front of the electrode surface, using the CFD-software package FIRE®. The simulation is based on different density values in the boundary layer at the electrode surface given by a density/concentration correlation. The copper concentration - linked with current density by the Faraday law - is solved by an additional transport equation. The thickness of diffusion layer and hydrodynamic boundary layer is calculated. The numerical solution of the fluid flow field is compared with results of LDA-measurements, which were done in a special cell parallel to the numerical calculation. The mathematically modeled copper concentration is also compared with experimental measurements. Furthermore, the limit current density is calculated for various values of the electrolyte circulation.

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A STUDY OF FLUID FLOW IN PACHUCA TANKS: D. A. Salinas G.[1]; *A. H. Castillejos E.*[1]; [1]Centro de Investigacion y Estudios Avanzados del IPN, Unidad Saltillo, Apdo. Postal 663, Saltillo, Coahila 25000 Mexico

Pachuca tanks are commonly used in the mineral processing industry for leaching operations. The velocity distribution in the liquid phase, resulting from the injection of gas into the draft tube, is important to achieve a complete suspension of the mineral particles and has a decisive influence in the mass transfer processes occurring in this reactor. This study investigated the effect of different design and operating characteristics on the liquid velocity field. Experiments were carried out in a laboratory-scale Pachuca tank. The transparent model was filled with water, and air was injected through the bottom to establish a recirculatory flow pattern in the absence of mineral particles. Liquid velocities for the whole reactor were measured under several experimental conditions using particle image velocimetry (PIV). This technique allowed to obtain a very detailed picture of the liquid motion even in the draft tube, when bubbles were absent from the measuring field of view. The experiments have shown that the liquid velocities increase with increasing the draft tube diameter to tank diameter ratio, the distance from the conical bottom to the draft tube entrance, or the gas superficial velocity. On the other hand, an increase in the water level with respect to the draft tube outlet causes a decrease of the liquid velocities in the tank.

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VISUALIZATION AND QUANTIFICATION OF THE FLUID FLOW IN A COPPER ELECTROWINNING CELL: *Gerhard Hanko*[1]; Klaus Hein[1]; Andreas Filzwieser[1]; [1]University of Leoben, Dept. of Nonferrous Metall., Franz-Josef-Straße 18, Leoben, Styria A-8700 Austria

Optical studies of the hydrodynamic flow in a copper electrowinning cell have been compared with experimentally determined velocity profiles. The experimental velocity measurements have been carried out in a laboratory cell using a laser Doppler anemometer. The relation between velocity profiles and the height measured from the lower edge of the electrodes has been examined for a constant current density. Moreover, the velocity distribution has been measured for a varied electrode interspace and different current densities. Each velocity profile has been evaluated with regard to the three different causes of the fluid flow: natural convection, forced convection by the electrolyte circulation and forced convection by the electrochemically induced gas stirring. The utilised software has made a calculation of the void fraction possible. Therefore, a rough estimation of the mass transfer coefficient through the prevailing gas bubble induced convection can be given, assuming influence of relative bubble volumina.

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OPERATION VARIABLES DESIGN ON SPIRAL HC 1870 AND HG 8/7 TO OPTIMIZE THE SEPARATION OF SILICE FROM IRON ORE THROUGH A MATHEMATICAL MODEL: *Mokka N. Rao*[1];

Asdrubal Serrano[1]; [1]Universidad Nacional Experimental De Guayana, U.N.E.G. Aptdo Postal 302, Puerto Ordaz 8015-A Venezuela S.A.

A mathematical model is developed which describes the movement of the minerals present where the vertical and angular velocities are related with the different operative parameters involved in the process of separation of silice from iron ore, which permit maximize the capacity of the spirals to obtain major productivity. The process is realized in two steps, of the rough dressing and the other cleaning. Through the results obtained for chemical analysis of the final products of each spiral and the equation of movement of the particles, it is proved the applicability and efficiency of mathematical model to operating parameters of the spirals. Moreover, it is determined through the recuperation of the final products of quality in the use of spirals HC 1870 and HG-8/7.

FUNDAMENTALS OF LEAD AND ZINC EXTRACTION AND RECYCLING: Recovery of Lead and Zinc From By-Products

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

Thursday AM Room: 7A
March 4, 1999 Location: Convention Center

Session Chairs: Arthur E. Morris, Thermart Software, San Diego, CA 92128-2720 USA; Markus A. Reuter, Technical University Delft, Dept. of Raw Mats. Proc., Delft 2628 RX The Netherlands

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THE REDUCTION OF ZINC OXIDE IN CALCIUM FERRITE SLAGS: *Hurman Rauf Eric*[1]; E. A. Van Dijk[1]; Markus A. Reuter[1]; [1]Delft University of Technology, Faculty of Applied Earth Sciences, 120 Mijnbouwstraat, Delft 2628 RX The Netherlands

Dusts from steelmaking processes contain substantial amounts of zinc. Such dusts are also a hazardous waste and dumping them becomes unacceptable from an environmental point of view. Therefore processes that can recover zinc and possibly other metals from steelmaking dusts are being investigated. The aim of this paper is a contribution to the more fundamental kinetic aspects of zinc reduction from silica-free calcium ferrite slags. The effects of alumina, lime and magnesium oxide contents of the slag, the CO/CO_2 ratio and the effect of initial Fe_2O_3CaO ratio were studied experimentally at 1400°C. The results indicated that the reduction of zinc from molten slag was possibly a first order reaction. As expected higher CO/CO_2 ratios increased both the extent and rate of reduction. It was also observed that a higher iron content of the slag improved the reduction of zinc from calcium ferrite slags. This fact seems to support the proposed mechanism that zinc is partly reduced by ferrous iron to zinc vapour and that ferric iron is reduced by carbon monoxide. The reduction rate of zinc oxide in these slags was decreased by increasing alumina content of the slag. Alumina decreased the calculated optical basicity of the slag showing the fact that reduction of zinc oxide was more favorable in more basic slags. Probably the formation of complex ions by alumina and zinc oxide such as $ZnAl_2O_3^{2+}$ lowers the activity of Zn^{2+} ions in the slag and hence renders them more difficult to reduce.

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FUMES, FOGS AND MISTS, PART 2: OPERATIONAL EXPERIENCE IN PYROMETALLURGICALLY RECOVERING ZINC AND LEAD FROM STEEL MILL DUSTS: *Larry M. Southwick*[1]; [1]L.M. Southwick & Associates, Suite 306, 992 Marion Ave., Cincinnati, OH 45229 USA

Baghouse dusts generated by integrated steel mills and electric arc furnace minimills contain economically interesting quantities of zinc and lead. A number of pyrometallurgical processes have been attempted in the past and new ones are being proposed to fume the heavy metals and recover them as liquid metals in a splash condenser. While splash condensers have long been demonstrated commercially in the zinc industry, their application to powdery, halide-containing steel mill dusts have uniformly met with difficulties. Part 1 of this paper reviewed theoretical and practical considerations in the design and application of splash condensers to this service. This paper, Part 2 of the series, will sumarize actual operation of two of these units and present a technical analysis of results and performance. The focus will be on condensation and collection efficiency of the units and an analysis of operating problems with the units. Of particular interest is recovery and recycling of heavy metals not collected i n the condenser, how that activity influenced earlier data analysis and the design of possible improvements, and an evaluation of those new designs in the light of these earlier operations. These specific results will also be related to the more general analysis presented in Part 1 of the study.

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RECYCLING OF GALVANIZED STEEL SCRAP USING CHLORINATION: *James K. S. Tee*[1]; Derek J. Fray[1]; [1]University of Cam bridge, Department of Materials Science and Metallurgy, Pembroke St., Cambridge, Cambridgeshire CB2 3QZ UK

The steel industry is facing a daunting task. It has become increasingly difficult to obtain clean scrap for the manufacture of steel. This problem has been accentuated by the use of galvanized steel. Present methods such as caustic leaching used for removal of zinc from steel scrap are not only tedious and costly but also unsuitable when zinc is present as an alloy. Based on a thermodynamics study, it is apparent that zinc chloride is more stable than zinc oxide while the reverse applies to the iron compounds. Described here, a novel separation route using air and chlorine mixtures has been proposed. Chlorine is both cheap and readily available; volatile chlorides are easy to separate, and better surface contact between gas and scrap can be achieved. This gives improved zinc removal over a shorter duration, with less preparation. Special attention, however, is required in handling chlorine due to its corrosive nature. The chlorination of galvanized steel in air and chlorine mixtures has been investigated in the laboratory by using thermogravimetry. Scanning electron microscopy, atomic absorption spectroscopy and x-ray diffraction were used to characterise the reaction products. The results demonstrated that it is feasible to separate zinc from steel at 800℃, using a ratio of 10: 1 with respect to air and chlorine. A separation of up to 97% zinc is achieved in 10 minutes. The chlorination of galvanized steel is based upon selective chlorination of zinc instead of iron. While zinc undergoes chlorination producing a volatile zinc chloride, the oxidation of iron provides a protective oxide layer of hematite that resists the attack of chlorine, and thus the carryover of iron as a chloride. This provides an attractive method for the steel related industries to recycle galvanized steel scrap.

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THERMAL TREATMENT OF JAROSITE: *I. Gaballah*[1]; A. Bonazebi[1]; N. Kanari[1]; [1]ENSG-LEM, Mineral Processing and Environmental Engineering, Rue du Doyen Marcel Roubault, BP 40, Vandoevre 54501 France

Jarosite contains up to 15% of heavy metals. The current waste disposal methods will not be allowed in the near future due to environmental regulations and pollution risks. For these reasons, thermal treatments of raw or decomposed jarosite, in controlled atmospheres, were investigated. The aim of these treatments is to decontaminate the jarosite and/or to recover the heavy metal compounds for recycling. According to physico-chemical characteristics of the samples, the thermal treatments under controlled atmospheres (N_2), (CO_2 + N_2) and (Cl_2 + air) lead to extraction extents that vary from 64 to 94%, from 89 to 98% and 95 to 99% respectively. Heavy metal compounds are separated by cooling the gaseous phase. The treatments' residue is almost free from heavy metal compounds. Between 700°C and 800°C, the chrlorination treatment was successful in eliminating more than 97% of heavy metal compounds contained in four different samples.

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SCALE-UP OF BIOLOGICAL REACTORS FOR SULFATE REDUCTION AND SULFIDE OXIDATION: *C. J. N. Buisman*[1]; G. H. R. Janssen[1]; H. Dijkman[1]; S. H. J. Vellinga[2]; [1]PAQUES Bio Systems B.V., P.O. Box 52, Balk 8560 AB The Netherlands; [2]PAQUES B.V., P.O. Box 52, Balk 8560 AB The Netherlands

THIOPAQ technology developed and marketed by PAQUES Bio Systems of Balk, Netherlands, has been successfully used at commercial scale at the Budelco zinc refinery in the Netherlands for the treatment of contaminated groundwater since 1992. In essence, THIOPAQ technology consists of two biological process steps in series: sulfate reduction to hydrogen sulfide (anaerobic) and sulfide oxidation to elemental sulfur (aerobic). The biogenic sulfide produced can be employed for the chemical precipitation of metals in solution either inside the anaerobic reactor or in a separate vessel. Since the solubilities of most metal sulfides are much lower than of their respective hydroxides, considerably lower effluent metal concentrations can be achieved with THIOPAQ systems than in neutralization processes which immobilize metals predominantly by hydrolytic precipitation. In recent years, PAQUES has made significant advances in the design and operation of aerobic and anaerobic bioreactors for metal-sulfur systems. Moreover, the company has increased its technology portfolio to allow the development of more process oriented applications of THIOPAQ technology. A new PAQUES designed plant at Budelco treating both the zinc electrowinning bleed stream as well as the acid plant blowdown will be described in the present paper. Special emphasis is put on the scale-up of the gas lift loop bioreactors as selected for this Budelco project.

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REMOVAL OF LEAD FROM PROCESS SOLUTIONS: *M. K. Mohan*[1]; Ramana G. Reddy[1]; [1]University of Alabama, Department of Metallurgical and Materials Engineering, P.O. Box 870202, A-129 Bevill Building, Tuscaloosa, AL 35487 USA

Processing of lead from secondary sources is of primary importance not only for the conservation of resources but also clean environment. In the present investigation, studies were conducted on the removal of Pb from process solutions using zeolites. Effects of pH, time and type of zeolite viz., chabazite, mordenite, erionite, and clinptilolite on the removal of Pb from solutions was investigated. Rate of sorption was found to depend on the pH of the solution and about 99pct. recovery was observed at pH 6. Optimal conditions were established for the maximum recovery of lead from process solutions. Possible sorption mechanisms were proposed. Based on the theoretical and experimental observations a conceptual flow sheet was proposed for the recovery of Pb from process solutions.

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RECOVERY OF HEAVY METALS FROM ACID MINE DRAINAGE WASTEWATER - AN INTEGRATED PROCESS: Paulo F.M.M. Correia[1]; Celina M.L. Santos[1]; M. Teresa A. Reis[1]; Jorge M.R. de Carvalho[1]; [1]Instituto Superior Tecnico; Department of Chemical Engineering, Av. Rovisco Pais - 1096 Lisboa Codex, Portugal

Acid drainage waste water from abandoned mines (namely the ones processing complex sulphides ores) have often high contents of heavy metals, such as iron, zinc, copper, cadmium, manganese, lead and nickel due to natural leaching of the mines exhausted ores. The leaching is increased by the atmospheric air oxidation of the sulphides to sulphates with consequent formation of sulphuric acid. If iron is present in the wastewater, Thiobacillus ferrooxidans bacteria help to catalyze the process. Further oxidation of the heavy metals present in the ores also helps to decrease wastewater pH and to increase mine waste water leaching power. These leachates end up contaminating ground waters and consequently rivers, lakes and wells, being a threat to the environment. Physical means of curtailing mine drainage formation and discharge, e.g. ground water diversion and mine sealing, have not met with unqualified success. Currently, treatment of acid mine drainage effluents to protect receiving streams appears to offer the best environmental protecting measure. Alkaline chemical neutralization followed by air oxidation has been the most popular method of mine water treatment. However considering the world wide continuous lacking of natural resources, new treatment processes that allow to concentrate selectively the metals present in the acid mine drainage wastewaters in order to allow their recovery are urgently needed. In this paper an integrated process involving cementation, leaching, emulsion liquid membranes, biosorption and electrolysis is proposed to treat the acid mine drainage wastewater of Algares mine (Aljustrel region, Portugal). This effluent has the following average composition: iron (891 ppm), zinc (500 ppm), manganese (98 ppm), copper (49 ppm), cadmium (1.25 ppm) and lead (1.11 ppm). Each of these heavy metals content is above the maximum permitted by the Portuguese environmental law. Through the application of the proposed integrated process a selective recovery of zinc, lead, copper and manganese with enough purity to allow their commercialization can be achieved. From the process an aqueous stream with low heavy metal content enough to be discharged in the environment and a sludge containing iron hydroxide and manganese result. This sludge can be disposed in a landfill according to the Portuguese environmental law.

INTERNATIONAL SYMPOSIUM ON GAMMA TITANIUM ALUMINIDES: TiAl Alloys: Creep

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

Thursday AM — Room: 8
March 4, 1999 — Location: Convention Center

Session Chairs: Michael J. Mills, The Ohio State University, Columbus, OH 43210 USA; Birgir Karlsson, Chalmers University, Dept. of Eng. Metals, Goteberg SE-412 97 Sweden

8:30 AM INVITED PAPER

MICROMECHANISMS OF CREEP OF GAMMA-BASE TITANIUM ALUMINDES: *Fritz Appel*[1]; Michael Oehring[1]; P. J. Ennis[2]; [1]GKSS Research Center, Materials Research, Max Planck St., Geesthacht D-21502 Germany; [2]Forschungszentrum Juelich, IWE, Institut fuer Werkstofforsch, Juelich D-52425 Germany

Creep strength and rupture life are critical issues regarding high temperature applications of gamma base titanium aluminides. The mechanisms controlling these properties are not yet fully understood, partly due to the wide variety and complexity of microstructures. In addition, the long-term creep behaviour is not well characterized at modest stresses and temperatures even though these conditions are close to the intended design requirements. Therefore, long-term creep tests were performed on different two-phase TiAl alloys. Deformation processes were investigated by TEM on specimens crept at T = 700ϒ and sigma = 80 - 140 MPa for 6.000 - 10.000 hours. Accordingly the creep strength seems to be limited by significant structural changes of the lamellar constituents due to the emission of dislocations and the propagation of structural ledges. Potential metallurgical techniques to improve the creep strength will be discussed.

9:00 AM

CREEP MECHANISMS IN A NEAR-GAMMA TiAl-ALLOY WITH DUPLEX MICROSTRUCTURE : *Birgit Skrotzki*[1]; T. Rudolf[1]; G. Eggeler[1]; [1]Ruhr-University Bochum, Dept of Mech. Eng., Institute for Materials, Bochum 44780 Germany

Intermetallic near-g TiAl-alloys are candidate materials for high temperature applications due to their attractive properties (i.e. low density, high strength, good oxidation resistance). Single-phase g-alloys and fully lamellar alloys have been intensively studied in the last 10 years. Duplex alloys have received less attention although they show a

good compromise of properties such as strength, ductility, fracture toughness and creep resistance. The present work studies the creep behavior of a TiAl-alloy with duplex microstructure. In addition to the measurement and evaluation of creep data for component design, special emphasis was given to the microstructural evolution during creep of a near-g TiAl-alloy with duplex microstructure. The following basic processes have been identified as key elements of the overall creep deformation mechanism: (i) ordinary dislocation plasticity, (ii) twinning and (iii) dynamic recrystallization. These processes are coupled and jointly control the creep behavior of the material.

9:20 AM

CREEP DEFORMATION OF TiAl-Si ALLOYS WITH ALIGNED LAMELLAR MICROSTRUCTURES: *David Ray Johnson*[1]; Yosihiro Masuda[1]; Takamitsu Yamanaka[1]; Haruyuki Inui[1]; Masaharu Yamaguchi[1]; [1]Kyoto University, Dept. of Mat. Sci. & Eng., Yoshida Honmachi, Sakyo-ku, Kyoto 606-8501 Japan

Creep tests were conducted on materials from a model system where the orientation and lamellar spacing were both controlled. Ingots of Ti-43Al-3Si with an aligned gamma/alpha2 lamellar microstructure were grown from an appropriately oriented seed by the floating zone technique. The as-processed microstructure consisted of eutectic silicide particles embedded in a PST matrix. Post processing heat treatments were then used to produce materials with either a fine or coarse lamellar spacing. Tensile creep tests were conducted at 1023 K (180 to 240 MPa) and 1073 K (120 MPa) on the as-processed and heat treated materials. The results clearly indicate the beneficial effect of decreasing the lamellar spacing as an order of magnitude difference in the secondary creep rate was found between the two microstructures. In addition to the lamellar spacing, the results are also discussed in terms of the microstructural stability of the lamellar microstructure.

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CREEP BEHAVIOUR OF A FULLY LAMELLAR Ti-47Al-2Nb-2Cr ALLOY: *Marc Thomas*[1]; [1]ONERA, Dept. Materiaux Metalliques et Procedes, BP 72, Chatillon, Cedex 92322 France

The creep behaviour of a fully lamellar Ti-47Al-2Nb-2Cr alloy has been studied over the temperature range from 650ϒC to 900ϒC and with the initial stress range between 69 and 400 MPa. Moderate variations in the activation energy Q and in the stress exponent n have been observed as a function of the creep conditions. The initial ingot which was supplied by the Austrian company Böhler was found to exhibit a highly textured structure. Our aim was then to assess the effect of texture by using typically five different orientations of the lamellar grains with respect to the deformation axis. Depending on this orientation, different plastic modes have been observed by means of tensile and compressive tests. Creep properties are therefore very sensitive to the orientation of the columnar grains and of the lamellae. Attempts to correlate the deformation anisotropy either to the orientation of the columnar grains or to the orientation of the lamellae are presented.

10:00 AM

NEUTRON DIFFRACTION MEASUREMENTS OF INTERNAL STRAINS IN TiAl-BASED ALLOYS: *Bimal Kad*[1]; Hahn Choo[2]; Mark Bourke[2]; [1]University of California-San Diego, AMES-0085, UCSD, La Jolla, CA 92093-0085 USA; [2]LANSCE, Los Alamos National Laboratory, Los Alamos, NM 87545 USA

Recent advances in computational methodologies can now predict the microstructure sensitive development of intrinsic strains and stresses inside thick anisotropic Ti-Al based composites [1]. However, such predictions are largely uncorroborated because of the lack of experimental means to probe at sub surface levels (i.e., deeper than 100μm). Towards this end, neutron sources present the unique capability of probing deep within dense structural materials and composites, to provide a reliable calibrating measure for the numerical predictions. Currently, a combination of experimental -theoretical -computational tools is being employed for directly measuring and interpreting the development of internal stresses in two-phase TiAl+Ti3Al low symmetry composite materials. The low symmetry results in severe internal constraints and stresses which affect both constitutive response and material toughness (i.e. ductility and fracture resistance). We will present our initial results on the evolution of internal stresses during i) thermo-mechanical processing induced phase transformations and ii) deformation and subsequent in-service loading in two-phase TiAl+Ti3Al alloys. [1] B.K. Kad, M. Dao and R.J. Asaro, (1995) Philos Mag, 71, p.567-604.

10:20 AM INVITED PAPER

IMPORTANCE OF MICROSTRUCTURAL STABILITY TO CREEP STRENGTH OF FULLY LAMELLAR TiAl ALLOYS: Kohei Mizoguchi[1]; Ryuichi Yamamoto[1]; Gerhard Wegmann[1]; *Kouichi Maruyama*[1]; [1]Tohoku University, Dept. of Mats. Sci., Aoba-yama 02, Sendai 980-8579 Japan

In principle, refinement of lamellar spacing should improve creep strength of fully lamellar TiAl based alloys. However, fine lamellar materials do not always give high creep strength, probably due to instability of fine lamellar structure during creep. High temperature creep of fully lamellar Ti-42mol%Al alloys with 0.1 and 1.5 micron meter in lamellar spacing was studied to examine effects of microstructural instability on creep strength. Microstructural degradation was more significant in the fine lamellar material at low stresses. Some specimens with the fine lamellar spacing were annealed at high temperatures to stabilize their lamellar structure. This heat treatment suppressed the microstructural degradation during creep, and improved creep strength of the fine lamellar material at low stresses. On the basis of these findings, it will be proposed that stable lamellar structure as well as fine lamellar spacing is highly important to improve long-term creep strength of fully lamellar TiAl alloys at low stresses.

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ON THE ROLE OF INTERFACE STRENGTHENING IN LAMELLAR MICROSTRUCTURES AT CREEP TEMPERATURES IN Ti-(47-48)Al BASED ALLOYS.: *Gopal Babu Viswanathan*[1]; Perena I. Gouma[1]; Subramanian Karthikeyan[1]; *Young-Won Kim*[2]; *Michael J Mills*[1]; [1]The Ohio State University, Dept. of Mats. Sci. and Eng., 477 Watts Hall, 2041 College Rd., Columbus, OH 43210 USA; [2]UES, Materials & Processes Division, 4401 Daton-Xenia Rd., Dayton, OH 45432 USA

Lamellar microstructures have traditionally shown higher creep resistance in g-TiAl based alloys. The strengthening in these microstructures comes from the presence of numerous g/g and g/a2 interfaces providing resistance to slip both in soft mode and hard mode type deformation. In this study, the presence of such interfaces in large numbers or in other words the decrease in inter-lamellar spacing has been observed to moderately decrease both the primary and secondary the creep rates in the temperature range 700-815ϒC, in polycrystalline binary Ti-48Al alloy studied. On the other hand, the creep rates are further lowered in Ti-47Al alloy containing C and Si. The strengthening here comes from the carbide and silicide precipitates at lamellar interfaces. Such lamellar interfaces have also been investigated in prior-to and post creep deformed samples. Defect analysis through weak beam dark field imaging was carried out to elucidate the dislocation mechanisms at the lamellar interfaces. Observations indicate that both 1/2[110] unit and <011] and [112] superdislocations are active, that the deformation is highly anisotropic and that the precipitates at these lamellar interfaces obstruct slip both in soft mode and hard mode orientations. A relative high density of mobile dislocations at the lamellar interfaces seem to suggest that the creep strain is controlled by the soft mode type deformation. Consequently, the presence of these precipitates play a major role in obstructing such interfacial slip by providing Orowan type strengthening at lower temperatures and/or providing climb barrier resistance at higher temperatures, similar to that of dispersion strengthened materials. However, these advantages of interface strengthening could be compromised by virtue of the instability of these interfaces caused by the dissolution of a2 during creep that has been seen to occur in this study. The posterior changes in the morphology of the interfaces and associated deformation structures have been addressed.

11:10 AM

THE EFFECTS OF MINOR ALLOYING ADDITIONS AND MICROSTRUCTURE ON THE CREEP BEHAVIOR OF Ti-47Al: *Margaret Keller*[1]; D. Eylon[1]; [1]University of Dayton, 300 College Park, Dayton, OH 45469 USA

Microstructure and certain minor alloying additions have been found to significantly influence the creep behavior of TiAl alloys. However their effects have not been isolated. This paper presents the results of a

systematic study investigating the effect of lamellar lath spacings and minor alloying additions of Si and C on the creep behavior of Ti-47Al. For each composition heat treatments were developed to produce two fully lamellar alloys with two different lamellar spacings. The effects of alloying additions and lamellar lath spacing on primary and secondary creep were measured at 760ϒC and 207MPa. Preliminary results indicate that additions of carbon as well as a refinement in lamellar spacing have beneficial effects on the creep behavior of this alloy.

11:30 AM

EFFECT OF FULLY LAMELLAR MORPHOLOGY ON THE CREEP OF A NEAR GAMMA TiAl INTERMETALLIC: Xiaomei Du[1]; *Jonathan Beddoes*[2]; Linruo Zhao[1]; [1]National Research Council of Canada, Structures, Materials & Propulsion Lab., Institute For Aerospace Research, Montreal Rd., M-13, Ottawa, Ontario K1A 0R6 Canada; [2]Carleton University, Dept. of Mech. & Aero. Eng., 1125 Colonel By Drive, Ottawa, Ontario K1S 5B6 Canada

The creep of Ti-48%Al with a fully lamellar microstructure is presented as a function of lamellar interface spacing and grain boundary morphology. The fully lamellar micro-structure is varied by altering the cooling from heat treatment in the a phase field, which included: furnace cooling, air cooling and an innovative two step cooling process consisting of furnace cooling followed by air cooling or water quenching. The lamellar interface spacing and extent of interlocked lamellae at grain boundaries increase with decreasing cooling rate. However, the two step process provides improved control of these microstructural features. Creep at 760ϒC/240 MPa indicates that the minimum creep strain rate decreases with decreasing lamellar spacing. Interlocked grain boundaries increase tertiary creep. The improved microstructural control available via the two step process allows the creep properties to be varied in terms of minimum creep strain rate and tertiary creep strain, providing a unique combination of creep properties.

11:50 AM

MICROSAMPLE TENSILE CREEP TESTING OF FULLY-LAMELLAR TiAl ALLOYS: *Carl J. Boehlert*[1]; *Mark Zupan*[1]; Dennis M Dimiduk[2]; Kevin J. Hemker[1]; [1]The Johns Hopkins University, Mech. Eng., 3400 North Charles St., Rm 122 Latrobe Hall, Baltimore, MD 21218 USA; [2]Materials and Manufacturing Directorate, Metals and Ceramics, Air Force Research Laboratory, Wright-Patterson AFB, OH 45433-7817 USA

Microsample Testing of single grains cut from polycrystalline metals has proven to be a valuable technique for understanding orientation effects and deformation behavior of titanium-aluminide alloys. An elevated-temperature microsample testing apparatus has recently been developed to better understand the creep performance of such alloys at targeted service temperatures. The present study focuses on the primary creep behavior of several TiAl alloys ranging in Al composition from 45-51(at.%). These alloys were thermomechanically processed and heat treated to obtain very large fully-lamellar grains containing different thicknesses of the alpha-2 and gamma phases. The objective of this work is to eliminate the effect of grain boundaries and characterize the primary creep deformation as a function of lamellar volume fraction, thickness, and orientation. The shapes of the primary transient will be modeled and, where possible, compared with microstructural observations of the underlying deformation mechanisms.

12:10 PM

MICRO- AND MACRO-MODELLING OF THE CREEP BEHAVIOUR OF TiAl ALLOYS: *Philippe Bastid*[1]; *Leo Christodoulou*[1]; *Ian Perrin*[2]; [1]Imperial College of Science, Technology and Medicine, Dept. of Mats., Prince Consort Rd., London SW7 2BP UK; [2]European Gas Turbine, Mechanical Engineering Centre, Whetstone, Leicestershire LE8 6LH UK

Creep tests and microstructural investigations carried out on TiAl intermetallic alloys at 750ϒC (Ti-48Al-2Nb-2Mn and XD Ti-47Al-2Nb-2Mn-0.8%TiB2) have shown different types of fracture behaviour depending on the stress applied (trans- and inter-lamellar at high stress and much finer "granular" fracture at low stress). The observed fracture morphologies have been related to the microstructural transformation occurring during creep, which involve local recrystallisation and void formation. This behaviour has been modelled using FEM analysis at both the micro- and macro-scales. Modelling at the micro-scale yields qualitative information concerning the strains and stresses appearing within a "basic representative cell" of the microstructure for given global stress and strain. The local strains predicted are sufficient to induce recrystallization as observed in the test specimens. The macro-creep behaviour of the alloys has been modelled using a modification of the Cumulative Damage Model of Dyson and McLean, that allows the description of the 3 stages of creep. Our model includes a recrystallisation term that allows the description of the change in the microstructure and its concomitant effect on creep behaviour. It is thus possible to predict lifetime for a wide range of stresses with good reliability.

LONG TERM STABILITY OF HIGH TEMPERATURE MATERIALS: Stability of Refractory Metals, Titanium and Stainless Steels

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

Thursday AM — Room: 9
March 4, 1999 — Location: Convention Center

Session Chair: Todd C. Deragon, Special Metals Corporation, New Hartford, NY 13413-5392 USA

8:30 AM INVITED PAPER

ELEVATED TEMPERATURE STABILITY OF THE REFRACTORY METALS: *R. W. Buckman*[1]; [1]Refractory Metals Technology, P.O. Box 10055, Pittsburgh, PA 15236-0415 USA

The refractory metals (Nb, Ta, Mo and W) and alloys were investigated extensively for space nuclear power systems applications which required exposures to elevated temperature, liquid alkali metals and vacuum for times up to 10 years. Substantial investigations were conducted which studied the effect of these test environments, for times up to 26,000 hours and temperatures up to 1700°C, on the mechanical behavior of these materials. This paper will discuss the results of these investigations and present examples of the changes in microstructure and mechanical behavior resulting from the test exposures.

9:00 AM

EFFECTS OF OXYGEN PRESSURE ON THE OXIDATION BEHAVIOR OF VANADIUM-CHROMIUM-TITANIUM ALLOYS AT 700°C: *M. Uz*[1]; K. Natesan[2]; C. Fullenwider[1]; [1]Lafayette College, Chem. Engr. Dept., 341 AHE, Easton, PA 18042 USA; [2]Argonne National Laboratory, Energy Technology Division, Argonne, IL 60439 USA

We estimated the effects of oxygen pressure and temperature on the oxidation kinetics and microstructure of V and V-base alloys containing (in wt.%) 4 Cr-4 Ti, 5 Cr-5 Ti, 10 Cr, 10 Cr-5 Ti, and 15 Cr-5 Ti. Samples were made from 1-mm-thick sheet stock of each alloy and were annealed for 1 h at 1050ϒC before any further oxidation. Experiments were performed in environments containing 760, 160, 0.1, 5 X 10^{-4} and 5 X 10^{-6} torr oxygen at three or more temperatures ranging from about 350 to 700ϒC. Oxidation behavior of each alloy was modeled by using the data of weight change with time. Microstructural features, including grain size and scale morphology and thickness, were determined from metallographic examination of the cross-sectional area of each sample across its thickness. Microhardness profiles across the sample thickness were used to determine the depth of oxygen penetration, and to estimate the parameters of diffusion of oxygen. These results will be presented, and the effects of oxygen pressure on the oxidation kinetics

and microstructure of V and V-Cr-Ti alloys will be compared. Work supported by the U.S. Department of Energy, Office of Fusion Energy Research, under Contract W-31-109-Eng-38.

9:20 AM

EFFECT OF LONG TERM AGING ON THE MICROSTRUCTURAL STABILITY AND MECHANICAL PROPERTIES OF Ti-6Al-2Sn-2Zr-2Mo-2Cr: *Xiao-Dong Zhang*[1]; William Baeslack[1]; Dan Evans[2]; Hamish Fraser[1]; [1]The Ohio State University, Dept. of Mats. Sci. and Eng., 2041 College Rd., Columbus, OH 43210 USA; [2]Wright Patterson AFB, Materials Directorate, WL/MLLM, Dayton, OH 45433 USA

The microstructural development of Ti-6Al-2Mo-2Cr-2Sn-2Zr (Ti-6-22-22) alloys after long term aging heat treatment has been studied by scanning electron microscopy (SEM), conventional transmission electron microscopy (CTEM) and high resolution electron microscopy (HREM). It is found that secondary intermetallic precipitates, namely alpha 2 and silicites, are formed depending on the specific aging temperatures. Precipitation of these intermetallic compounds has strong effect on the fracture toughness and tensile properties of the alloys. Results on the macro and micro deformation modes associated with crack initiation and dislocation characteristics will be presented. The importance of these observations will be discussed in view of the fundamental understanding and further control of the structural stability of these type of a-b Ti alloys.

9:40 AM

PHASE STABILITY OF LAVES INTERMETALLICS IN STAINLESS STEEL-ZIRCONIUM ALLOYS: *Daniel P. Abraham*[1]; James W. Richardson[2]; [1]Argonne National Laboratory, Chemical Technology Division, Bldg. 205, Room A167, 9700 S. Cass Ave., Argonne, IL 60439 USA; [2]Argonne National Laboratory, Intense Pulsed Neutron Source, 9700 S. Cass Ave., Argonne, IL 60439 USA

Laves intermetallics in the stainless steel - 15 wt% zirconium (SS-15Zr) alloy are metastable and transform to the Zr6(Fe,Cr,Ni)23 intermetallic during high-temperature annealing. The growth of the Zr6(Fe,Cr,Ni)23 intermetallic has been studied by in-situ high-temperature neutron diffraction. The as-cast SS-15Zr alloy contains the stainless steel phases, ferrite and austenite, the Laves intermetallics C36 and C15 and small amounts of Zr6(Fe,Cr,Ni)23. Neutron diffraction patterns as a function of time have been obtained on SS-15Zr alloys that were held at various elevated temperatures. Phase transformation was very slow for temperatures < 1150ϒC. Alloys held at temperatures between 1200-1250ϒC showed diffraction peaks corresponding to ferrite, C15 and Zr6(Fe,Cr,Ni)23 after extended annealing times. We will discuss the results of results of neutron diffraction analysis and propose a mechanism for Zr6(Fe,Cr,Ni)23 formation.

10:00 AM

LONG TERM CREEP RUPTURE PROPERTIES AND PRECIPITATION IN TYPE 316 STAINLESS STEELS: *Takanori Nakazawa*[1]; Yasuo Otoguro[1]; Hidetaka Kimura[2]; Hitoshi Kaguchi[3]; Manfred Schirra[4]; [1]Gunma University, Mech. Syst. Eng., 1-5-1 Tenjin-cho, Kiryu, Gunma 376-8515 Japan; [2]Nippon Steel Corporation, Steel Research Labs., 20-1 Shintomi, Futtsu, Chiba 293-8511 Japan; [3]Mitsubishi Heavy Industries, Ltd., Nuclear Plant Engineering, 1-1 Wadasaki-cho, Hyogo-ku, Kobe, Hyogo 652-8585 Japan; [4]Forschungszentrum Karlsruhe, Institute fur Materialforschung 1, Postfach 3640, Karlsruhe D76021 Germany

The knowledge about the relationship between creep rupture properties and microstructure is required to estimate the long term creep behavior. The microstructure of Type 316 steels with different carbon and nitrogen contents tested in creep rupture at 550ϒC and 600ϒC up to 40000h has been examined with electron microscope. All steels had the same rupture strength at short rupture time. Low carbon medium nitrogen steel(LCMN) showed the highest strength at longer time and higher rupture ductility than the other two steels. In LCMN fine Laves phases precipitated on the grain boundaries(GB), while small amount of carbides and G phases precipitated on GB. Although medium carbon medium nitrogen steel(MCMN) showed the similar precipitation behavior on GB, the amount of carbides was a little larger than LCMN. Carbides and Laves also precipitated in the matrix of MCMN. In high carbon low nitrogen steel many carbides precipitated on GB and in the matrix whereas Laves appeared after longer period. The present results show that the creep rupture properties strongly depend on the precipitation behavior.

10:20 AM BREAK

10:30 AM

ELEVATED TEMPERATURE DIMENSIONAL STABILITY OF THIN GAUGE Fe-Cr-Al-RE (RARE EARTH) ALLOY FOR CATALYTIC CONVERTER SUBSTRATE APPLICATIONS: *Steve Chang*[1]; Bijendra Jha[1]; [1]Texas Instruments, Inc., Materials and Control, 34 Forest St., MS 4-14, Attleboro, MA 02703 USA

Honeycomb structures consisting of corrugated and flat ferritic Fe-20Cr-5Al-RE alloy foils have seen increased application as the substrate for stationary and automotive catalytic converters. The oxidation resistance of Fe-20Cr alloy is improved by the addition of Al which forms alumina scale to protect alloy substrate during elevated temperature exposure. The addition of rare earth elements, such as La and Ce, further improves cyclic oxidation resistance and enable the catalytic converter to satisfy the regulatory requirement for emission control. The major failure mode of honeycomb substrate during prolonged exposure at elevated temperature is the rupture of foil due to stretching. The necessary stress state in the honeycomb structure for stretching to occur is generally attributed to the dimensional change of alloy foils. This foil dimension has to remain constant in order for honeycomb structure to sustain long term, elevated temperature service. The elevated temperature dimensional change of Fe-20Cr-5Al-RE alloy foil was quantified by testing sub-size honeycomb samples. The effects of alloy chemistry on the oxidation rate and dimension change of Fe-20Cr-5Al-RE alloy foil are correlated and will be presented. A foil life prediction will be proposed and validated by testing foil with varying chemistry and gauges.

10:50 AM

ROLE OF REACTIVE ELEMENT ON LONG-TERM STABILITY OF ALUMINA SCALE FORMED ON Fe3Al DURING HIGH TEMPERATURE OXIDATION: *I. Kim*[1]; W. D. Cho[1]; [1]University of Utah, Dept. of Metall. Eng., Browning Bldg., Salt Lake City, UT 84112-1183 USA

A study on oxidation of iron aluminides was performed to investigate the effect of reactive element (yttrium) in terms of oxidation rate and oxidation adhesion at the temperature range of 800°-1100°C. At lower temperatures (<1000°C), oxidation rates of alloys, Fe_3Al and Fe_3Al-Y, was nearly same and alumina scale formed on the alloys displayed good adhesion. However, yttrium-added Fe_3Al alloy showed lower oxidation rate and much more improved oxide adhesion at higher temperatures. Microstructural examination of the oxidized Fe_3Al-Y alloy revealed the following: (1) formation of pegs at alumina scale/substrate interface, (2) formation of $Y_3Al_5O_{12}$ phase at the surface of the alumina scale, and (3) growth of alumina scale with preferred orientation. Adhesion improvement is believed to be due to the formation of pegs which increase the stability of the alumina scale. It was found that pegs were formed at grain boundary of the substrate near the interface because of the predominant diffusion of oxygen via grain boundary of lattice of alumina scale.

11:10 AM

REACTIONS BETWEEN THE COMPONENTS OF SOLID OXIDE FUEL CELLS AT 800-1000ϒC IN AIR: *Peter Majewski*[1]; Fritz Aldinger[1]; [1]Max-Planck-Institut für Metallforschung, PML, Heisenbergstr. 5, Stuttgart, 70569 Germany

Reactions between the different components of solid oxide fuel cells (electrolyte: ZrO2 or LaGaO3; cathode: LaMnO3; interconnector: LaCrO3) have been studied in detail for temperatures that are relevant for the application of the cells. A reaction between Y stabilized ZrO2 and Sr doped LaMnO3 has not been observed. However, diffusion of Mn into ZrO2 is significant. Sr doped LaMnO3 reacts with Sr as well as Mg doped LaGaO3 forming various products. Even a reaction between Sr doped LaMnO3 and Ca doped LaCrO3 has been observed for 1000ϒC in air. In addition, a decomposition of single phase Sr doped LaMnO3 into SrMnO3 and Sr poor LaMnO3 occurs at temperatures below about 1300ϒC in air.

11:30 AM

ISOTHERMAL OXIDATION BEHAVIOR OF TI-49AL ALLOY: *Xuerong Wen*[1]; *Ramana G. Reddy*[1]; [1]University of Alabama, Dept. of Metall. and Mats. Eng., Tuscaloosa, AL 35487 USA

The isothermal oxidation behavior of binary Ti-49Al intermetallic was investigated in pure oxygen over the temperatures of 750ϒC to 1000ϒC. The experiments have been carried out using TGA set up. The oxidation products were analyzed using X-ray diffraction, SEM and EDS. Parabolic rate constants were calculated. An effective activation energy of 404 kJ/mol was deduced. The oxidation products formed were identified as TiO2(rutile) and "-Al2O3 (alumina) at all experimental temperatures. The oxidation scale was more adherent compared to that of Ti-32Al. It was also observed that the layer structure was formed at 1000ϒC due to more rapid outward diffusion rate of Ti than that of Al. A physical model for layer structure formation was developed.

MATERIALS PROCESSING FUNDAMENTALS: Nonferrous

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

Thursday AM — Room: 5A
March 4, 1999 — Location: Convention Center

Session Chairs: Derek John Fray, University of Cambridge, Dept. of Mats. Sci. and Metall., Cambridge, Cambs CB23QZ England

8:30 AM

MECHANISM OF REFRACTORY WEAR BY CALCIUM FERRITE SLAG: *Hideya Sato*[1]; Fumito Tanaka[1]; Susumu Okabe[2]; [1]Mitsubishi Materials Corporation, Central Research Institute, 1-297 Kitabukuro-cho, Omiya, Saitama 330-8508 Japan; [2]Mitsubishi Materials Corporation, Naoshima Smelter and Refinery, 4049-1 Naoshima-cho, Kagawa-gun, Kagawa 761-3100 Japan

Refractory wear caused by melts is one of the major determining factors for the interval of shut-down repair of the metallurgical furnaces in general. Calcium ferrite slag, employed by Mitsubishi Continuous Copper Converter, shows high fluidity and corrosive characteristics against most of the refractories. In order to improve the corrosion resistance of the refractories, the mechanism of MgO-based refractory wear by the calcium ferrite slag was intensively studied. The dissolution behavior of the refractory into the molten slag and the penetration of the molten slag into the refractory were observed by crucible tests and newly developed oscillating furnace tests. It was found that the wear of MgO-based refractories by the calcium ferrite slag is mainly dominated by the internal structural failure caused by the penetration of CaO-Cu2O rich slag which is formed as a result of the preferential absorption of FeOx from original slag by the spinel of the refractory.

8:55 AM

A DYNAMIC ELECTROCHEMICAL TECHNIQUE FOR THE MEASUREMENT OF TRACE AMOUNTS OF ARSENIC AND ANTIMONY IN MOLTEN ZINC: *Derek J. Fray*[1]; Terry E. Warner[1]; [1]University of Cambridge, Materials Science and Metallurgy, Pembroke St., Cambridge, Cambs CB2 3QZ England

In order to detect arsenic and antimony in zinc various electrochemical experiments were performed involving the electrochemical introduction of sodium atoms into molten zinc using a solid electrolyte. Under high rates of the formation of the intermetallic phase NaZn13 was observed. Under more moderate injection rates employing a symmetric "zinc/zinc cell" configuration, a qualitative relationship between the current generated during cyclic voltammetry and the arsenic and antimony concentrations in molten zinc was observed.

9:20 AM

DYNAMIC PROCESS SIMULATION OF CONTINUOUS COPPER SMELTING FURNACE: *Osamu Inoue*[1]; Susumu Okabe[2]; [1]Mitsubishi Materials Corporation, Central Research Institute, 1-297 Kitabukuro-cho, Omiya, Saitama 330-8508 Japan; [2]Mitsubishi Materials Corporation, Naoshima Smelter and Refinery, 4049-1 Naoshima-cho, Kagawa-gun, Kagawa 761-3100 Japan

In Mitsubishi Continuous Copper Smelting and Converting Process, smelting, slag-matte separation and matte converting are continuously carried out in series in three furnaces connected by launders. And there influence of the change in operating condition in upper stream, such as variation of feeds in the smelting furnace, propagates to down stream with some delay. In order to achieve stable operation, process control algorithm based on the dynamic characteristics of each furnace would be very effective. In this study, the dynamic process simulation model was developed for the smelting furnace. The model consists of two mathematical modules, i.e. the thermodynamic module and the mixing module. The calculation results using operating data of charged materials, i.e. concentrates, fluxes, coal, oxygen, air, etc., obtained from Naoshima Smelter showed good agreement with the actually observed change in temperature, composition and flow rate of matte and slag at the outlet of the furnace. In addition, operation parameters such as reaction efficiency of oxygen and coal, dead volume of melts were estimated.

9:45 AM

THERMAL DECOMPOSITION OF ENARGITE: *R. Padilla*[1]; Y. Fan[1]; I. Wilkomirsky[1]; [1]University of Concepcion, Department of Metallurgical Engineering, Edmundo Larenas, Concepcion 270 Chile

In most of the Chilean copper and gold concentrates, arsenic is present mainly as enargite, Cu_3AsS_4 which at the conventional roasting or smelting temperature decomposes liberating arsenic compounds. The objective of this investigation was to study the decomposition reaction of energite in an inert atmosphere in the range of 530ϒC-750ϒC. The effect of the particle size on the decomposition reaction was also investigated. The results obtained indicated that the decomposition starts at about 550ϒC. Two distinct regions in the temperature dependence of the decomposition rate were observed; a low temperature region between 550ϒC to 650ϒC and a high temperature region between 560ϒ to 750ϒC. The X-ray diffraction analysis suggests that the decomposition of enargite occurs through the formation of intermediate tenantite, according to the following sequential reactions; $4Cu_3S_4(s)$ - Cu_{12} $As_4S_{13}(s)$ + 3 /$2S_2(g)$; $Cu_{12}As_4S_{13}(s)$ - $6Cu_2S(s)$ + $2As_2S_3(g)$ + $1/2S_2$(g. The kinetics of the decomposition was analyzed by using the model for a topochemical reaction of spherical particles. $1-(1-X)^{13}$-kt, which represented well the data. Apparent activation energies of 612 kJ/mol and 110.9 kJ/mol were found for the low and high temperature regions, respectively.

10:10 AM BREAK

10:20 AM

VIRCOSITY OF HIGH MAGNESIUM CONTENT FeO-Fe_3O_4-SiO_2-CaO-MgO SLAGS AT NICKEL SMELTING CONDITIONS: *Tan Pengfu*[1]; Zhang Chuanfu[1]; Zeng Dewen[1]; Li Zuogang[1]; Ari Jokilaakso[2]; Tapio Ahokainen[2]; [1]Central South University of Technology, Department of Nonferrous Metallurgy, Changsha 410083 China; [2]Helsinki University of Technology, Lab. of Materials Processing and Powder Metallurgy, FIN-02015, Hut, Espoo PB 6200 Finland

The viscosity of high magnesium content FeQ-Fe_3O_4-SiO_2-CaO-MgO slags at nickel smelting conditions was investigated using a commercial rotational viscometer. The studied parameters were composition of slag and temperature. The viscosity of these slags was measured as a function of CaO, MgO, SiO_2 Fe and Fe/SiO_2 in temperature range from 1473K to 1723K. These slags contained 5.81 to 10.59 pet MgO, 0 to 10.37 pct CaO, 28.21 to 36.21 pet SiO2, 39.40 to 55.42 pet Fe and 1.1 to 1.5 Fe/SiO_2.

10:45 AM

FLAME ATOMIC ABSORPTION ANALYSIS OF GOLD JEWELLERY: *M. A. Llavona*[1]; M. C. Crespo[1]; A. M. Fernandez[1]; J. L. Ibanez[1]; R. Zapico[1]; [1]University of Oviedo, Dept. Materials Science, U.S. of Mining and Topographhic Engineering, Reinerio garcia s/n, Mieres 33600 Spain

In Spain, as in many countries, the gold content of jewellery must be officially hallmarked. The official methods of assay are gravimetric cupellation (a method which is highly accurate but both time and sample consuming), potentiometry, gravimetry and volumetry. In this paper, a procedure for measuring gold by flame atomic absorption in jewellery samples is described. The method is based on the acid digestion of a 40 mg sample. The quantity of aqua regia necessary for dissolving the gold, the ideal weight of a sample in order that the error may be minimal, the effect of the acids employed, the type of material used for its storage, and the necessity of employing a buffer to avoid the ionization of the solution are described. The method proposed is simple, highly accurate and causes little damage to the jewellery.

11:10 AM

THERMODYNAMIC MODELING FOR THE EVALUATION OF THE CO-PRODUCTS BEHAVIOR IN THE NICKEL/COPPER SMELTING AND CONVERTING PROCESSES: *Florian Kongoli*[1]; [1]FLOGEN Technologies, 306-3325 Edouard Montpetit Montreal, Quebec H3T 1K4 Canada

The behavior of the co-products and byproducts in the Ni/Cu smelting and converting processes effects directly the quality of the final products as well as the revenues gained from the overall process. An effective way to evaluate and predict this important behavior is thermodynamic modeling. This work presents the thermodynamic modeling of various phases in Ni/Cu smelting and converting processes and shows how these can be used to predict and evaluate various aspects of this behavior such as the activities of different components in the matte phase, matte-slag distribution, metal-slag distribution, etc. Future developments are also discussed.

11:35 AM

PROGRESS IN UNDERSTANDING COPPER ANODE SLIMES SMELTING: S. Neven[1]; D.R. Swinbourne[2]; B. Blanpain[1]; [1]Department of Metallurgy & Materials Engineering, Catholic University of Leuven, De Croylaan 2, B-3001 Leuven, Belgium; [2]Department of Chemical & Metallurgical Engineering, RMIT University, P.O. Box 2476V, Melbourne, 3001, Australia

The smelting of copper anode slimes, a material which contains mostly lead, silver, copper and selenium, has been practiced for many years with a view to recovering the silver and associated small amounts of gold. However, a theoretical understanding of the process has been lacking and this handicaps efforts to improve and intensify smelting operations. In the past few years work has been done in this area and this work will be reviewed in the paper. The underlying thermodynamics of the oxidation of silver-copper selenide mattes has been developed and used as a basis for the construction of a computational thermodynamics model which attempts to predict the composition of all condensed phases during the course of smelting. The model will be outlined and its successes in matching experimental data, as well as its current deficiencies, will be considered. Supporting work on the thermodynamics of silver solubility in slags, on activity-composition relationships in the Ag-Se system and work in progress on the oxidation state of copper in the slags will be reviewed. These projects are designed to provide further detailed data which will improve the robustness of the thermodynamic model.

MICROMECHANICS AND MICROMECHANISMS OF DEFORMATION AND FRACTURE: A SYMPOSIUM IN HONOR OF PROFESSOR ALI S. ARGON: Ali S. Argon Symposium VII

Sponsored by: Structural Materials Division, Mechanical Metallurgy Committee, High Temperature Alloys Committee

Program Organizers: K. Jimmy Hsia, University of Illinois, Dept. of Theor. & Appl. Mech., Urbana, IL 61801 USA; Mary Boyce, Massachusetts Institute of Technology, Dept. of Mech. Eng., Cambridge, MA 02139 USA; Tresa M. Pollock, Carnegie Mellon University, Dept. of Metall. Eng. & Mat. Sci., Pittsburgh, PA 15213 USA

Thursday AM — Room: 14B
March 4, 1999 — Location: Convention Center

Session Chair: K. Jimmy Hsia, University of Illinois at Urbana-Champaign, Dept. of Theor. & Appl. Mech., Urbana, IL 61801 USA

8:30 AM

MECHANICAL AND MICROSTRUCTURAL PROPERTIES OF NOTCHED E-GLASS/VINYL ESTER COMPOSITE MATERIALS SUBJECTED TO THE ENVIRONMENT AND A SUSTAINED LOAD: *Stephanie E. Buck*[1]; David W. Lischer[1]; *Sia Nemat-Nasser*[1]; [1]University of California, San Diego, Center of Excellence for Advanced Materials, 9500 Gilman Drive, La Jolla, CA 92093-0416 USA

Flaws may be created in composite materials during manufacturing, machining, or use. Composites with such flaws, when subjected to adverse environmental conditions in the presence of a sustained load, may have dramatically reduced mechanical properties and changes in their microstructural properties up to failure. E-glass/vinyl ester composite coupons with a single edge flaw have been conditioned for periods up to 3000 hours at room temperature and at elevated temperatures, with and without a sustained load, to determine the changes in the tensile properties and damage mechanisms which occur with the introduction of the flaw. Several fiber architectures have been studied. The tensile strength has been found to decrease by at least fifteen percent for notched samples when compared with unnotched samples subjected to the same environmental and load conditions. The early damage mechanisms have been found to change from transverse matrix cracking, fiber breakages, and occasional edge delaminations for unnotched specimens to the growth of a significant matrix crack from the notch tip and well-defined internal delaminations for notched specimens. The notched specimens have been analyzed using a finite element model as well as existing constitutive relations.

8:50 AM

COMPACTION OF WOVEN FABRIC PREFORMS IN COMPOSITE MOLDING PROCESSES: *Tsu-Wei Chou*[1]; Baoxing Chen[1]; [1]University of Delaware, Center for Composite Materials and Department of Mechanical Engineering, Newark, DE 19716-3140 USA

Fiber composite materials based upon 2D and 3D textile preforms have received considerable attention in recent years. The merits of fabric composites include ease of fabrication, cost-effectiveness, and enhanced properties in the thickness direction. Among various composite manufacturing techniques, liquid composite molding processes, such as resin transfer molding, and resin film infusion process are of very high potential. While the preforming processes, such as weaving, knitting, braiding and stitching, orients the fibers into a skeleton of the actual part, the final fiber microstructure depends to a certain extent on the compaction of the preform to the desired thickness. The compaction of a preform due to tool closure and vacuum bagging flattens the

yarn bundles, reduces the pores and gaps among the fibers and yarns, and results in elastic deformation, nesting and inter-layer packing. All these factors enhanced the overall composite fiber volume fraction. This paper reports our recent research in the development of analytical models and methodologies for predicting the compaction behavior of woven fabric preforms in order to provide better guidance for engineering design and manufacturing of fabric composites by liquid composite molding and resin film infusion processes. The analysis focuses on the unit cell of an othogonal plain weave fibrous preform, which is composed of two sets of mutually orthogonal yarns of the same fiber (non-hybrid fabric). A 3D model of the unit cell is proposed with certain simplifying assumptions to predict the compressive behavior of yarns. Yarn nesting, yarn cross-section deformation, yarn flattening and yarn elastic deformation are considered in this analytical model. Based upon the proposed model and the beam theory in the mechanics of materials, analytical expressions for the relations among fiber volume fraction, applied compressive force and preform thickness reduction are established. Results of analytical predictions are compared with experiments. The implication of the present study on the understanding of preform permeability is also discussed.

9:10 AM

THE MONOTONIC AND FATIGUE BEHAVIOR OF CONTINUOUS FIBER-REINFORCED CERAMIC-MATRIX COMPOSITES (CFCCS) : *Naren Miriyala*[1]; Peter K. Liaw[2]; Carl J McHargue[2]; Lance L Snead[3]; [1]Solar Turbines, Inc., P.O. Box 85376, MZ R-1, San Diego, CA 92186-5376 USA; [2]The University of Tennessee, Materials Science and Engr., 434 Dougherty Engineering Building, Knoxville, TN 37996 USA; [3]Oak Ridge National Laboratory, Metals and Ceramics Division, P. O. Box 2008, MS 6087, Oak Ridge, TN 37831-6087 USA

Monotonic and fatigue tests were performed at room temperature in air, and at 1000ϒC in argon environment, on two continuous fiber reinforced ceramic matrix composites (CFCCs), namely, Nicalon/Alumina and Nicalon/SiC composites. Flexure specimens were used to perform the mechanical tests. The loads were applied either parallel or normal to the fabric plies to study the effects of fabric orientation to the loading axis on the mechanical behavior. The monotonic and fatigue behavior of the Nicalon/Alumina composite was significantly affected by the fabric orientation at room temperature and 1000ϒC, while the effects were insignificant in the Nicalon/SiC composite. The damage mechanisms responsible for the observed effects will be the focus of the paper. The results of finite element analysis (FEA) also will be presented to explain the effects of fabric orientation on the flexural behavior of laminate composites. Research supported by DOE under a subcontract from Lockheed Martin Energy Corporation (No. 11X-SV483V) to the University of Tennessee.

9:30 AM

FRACTURE TOUGHNESS AND HYDROGEN-ASSISTED CRACKING OF FORGED 304L AND 316L STAINLESS STEELS: *Brian P. Somerday*[1]; Neville R. Moody[1]; Ben C. Odegard[1]; Steve L. Robinson[1]; [1]Sandia National Laboratories, Materials Reliability Dept., P.O. Box 969, MS 9403, Livermore, CA 94551 USA

Severe localized deformation can develop during forging of stainless steel components into complex shapes, which produces microstructures characterized by elevated strength as well as elongated and recrystallized grains. The fracture behavior of such stainless steel microstructures formed from high deformation at elevated temperature has not been extensively investigated in as-forged components, particularly in hydrogen environments. This work characterizes the fracture toughness and hydrogen-assisted crack growth of 304L and 316L stainless steels that were forged to high strain levels (50% to 75%), which produced elevated-strength (greater than 500 MPa) microstructures that varied in degree of recrystallization (up to 100%) and grain aspect ratio (up to 4:1). Compact tension specimens were tested at room temperature in the as-forged condition and after charging in 140 MPa hydrogen gas at 300ϒC (equilibrium hydrogen concentrations between 0.4 - 2 at.%). Additional experiments involved constant-displacement loading of WOL specimens in 200 MPa hydrogen gas at room temperature. Mechanisms of fracture in the as-forged and hydrogen-exposed conditions are interpreted based on analysis of fracture surfaces coupled with models of ductile fracture and hydrogen embrittlement. Supported by the U.S. Dept of Energy under contract # DE-AC04-94L85000

9:50 AM BREAK

10:00 AM

DYNAMIC COMPRESSION FATIGUE OF IN-SITU REINFORCED SILICON NITRIDE AT ELEVATED TEMPERATURES - FAILURE MECHANISMS: *Gayathri Raghavendra*[1]; Sia Nemat-Nasser[1]; Mingqui Liu[1]; [1]Univeristy of California, San Diego, Center of Excellence for Advanced Materials, 9500 Gilman Drive, La Jolla, CA 92093-0416 USA

Silicon nitride is a promising candidate material for high temperature structural applications on account of its high strength and toughness up to elevated temperatures, good creep resistance, low density, low coefficient of thermal expansion and good corrosion and oxidation resistance. In order to use the material for high temperature structural applications, its quasi-static and dynamic fatigue properties need to be evaluated over a range of temperatures. This paper focuses on the dynamic compression fatigue of in-situ reinforced silicon nitride over a range of temperatures from room temperature to 1000ϒC. The unique experimental facilities that have been developed in order to conduct high strain rate tests at elevated temperatures will be described. Novel techniques that have been developed to accurately measure strains in hard ceramics [like silicon nitride] will also be presented. A detailed discussion of the experimental results obtained from high strain rate tests conducted using the Enhanced UCSD Hopkinson Bar Technique over a range of temperatures will be given. In addition, the results of microstructural analysis, including Scanning Electron Microscopy, Transmission Electron Microscopy, High Resolution Transmission Electron Microscopy and X-Ray Diffraction, on as-received material as well as tested material will be presented. Finally, the mechanisms of fatigue crack growth in in-situ reinforced silicon nitride and the toughening mechanisms will be discussed.

10:20 AM

DYNAMIC BEHAVIOR OF SiC UNDER UNIAXIAL COMPRESSION.: *Sai Sushilkumar V. Sarva*[1]; Sia Nemat-Nasser[1]; [1]University of California, San Diego, Center of Excellence for Advanced Materials, 9500 Gilman Drive, La Jolla, CA 92093-0416 USA

SiC is used in important impact related applications, such as integrated armor. This necessitates development of constitutive models which describe its mechanical behavior. Experimental results which relate the strain rate to the compressive strength of SiC under uniaxial loading are obtained. Quasi-static tests are conducted using a servo-hydraulic Instron universal testing machine. Dynamic tests are performed using a modified split-Hopkinson pressure bar. It is seen that there is a marked increase in compressive strength at strain-rates higher than 10^2/s. The failure modes are similar in specimens loaded at both low and high strain rates. At peak stress these specimens fail by axial splitting. This paper compares the experimental results to those predicted by a simple model of interacting, dynamically growing wing cracks which coalesce to cause failure of a brittle solid.

10:40 AM

MICROMECHANISM OF BRITTLE FRACTURE IN MEDIUM CARBON MICROALLOYED STEELS: *Djordje Drobnjak*[1]; Husain Hraam[1]; [1]University of Belgrade, Faculty of Tech & Metall, Karnegijeva 4, P.O. Box 3503, 11120 Belgrade Yugoslavia

The relationship between microstructural parameters and cleavage fracture has been studied in (950-1300 $_0$ C) air cooled V-microalloyed steels by means of impact testing, light microscopy and scanning electron microscopy. Large variation in impact energy are obtained as a function of test temperature and microstructure. The results show that acicular ferrite (AF) and a multi-phase structure consisting of ferrite-pearlite (FP) and 30-70% AF possess room temperature toughness superior to that of classical bainitic sheaves, (BS) as revealed by impact energy level. However, AF is superior to FP-AF in terms of energy transition temperature. At liquid nitrogen temperature, all steel grades show similar behavior. Transganular cleavage is an exclusive mode of fracture. Primary brittle nuclei, which control the critical tensile strength for fracture, σ_F, are found to be brittle TiN particles of diameter >2μm.

Large TiN particles are friendly, because the cracks are initiated by stress much smaller than that required for crack progagation. This means that cracks will become blunted out, what will make them inactive before the stress for crack propagation is achieved. Carbides and martensite/austenitc/carbide MAC consituent are tentatively identified as secondary brittle fracture nuclei, but they are of less significance. As the critical stage of brittle fracture is crack propagation through particle/matrix interface, the morphology and ferrite grain size play little role. Calculation of maximum tensile stress below the notch, σ max, and critical tensile strength for fracture, σ F, under assumption that the diameter of TiN particle, which are the primary nuclei, are equal to penny shaped crack size, have shown that the requirements for crack propagation through particle/matrix interface, $\sigma_{max} > \sigma_F$, is satisfied from the beginning of fracture process at liquid nitrogen temperature in all steels studied in this work. Room temperature behavior of these steels is considerably different. The dominant fracture mechanism is still transgranulur cleavage, but this preceded by a lower (BS steels) or higher (AF steels) degree of ductile fracture. Calculations have shown that at the beginning of fracture $\sigma_{max} < \sigma_F$. This means that the brittle crack initiated in brittle particles can not propagate; instead, the ductile crack will be initiated and propagated. During propagation, ductile crack is assumed to accelerate, what, in turn, increases the strain rate, and consequently, σ_Y and σ_{max}. At a critical ductile crack length, critical condition: $\sigma_{max} > \sigma_F$ is achieved, and brittle cracks, initiated in brittle particles ahead of the ductile crack tip are activated. These progagate across particle/matrix interface and cause the fracture. Higher toughness of steels with AF structure requires a longer ductile crack to be formed, than in steels with BS structure, before requirement for brittle fracture, $\sigma_{max} - \sigma_Y * n > \sigma_F$ is attained, because the strain hardening exponent (n) of the former steel is much lower and the product $\sigma_Y * n$ is smaller in spite of σ_Y is higher. The overall contribution of ductile fracture to the toughness is relatively small because the shear decohesion mechanism, which dominates ductile fracture in both steels, is characterized by a low expenditure of energy. In spite of TiN inclusions are present, the primary nuclei are assumed to be carbides, smaller than 1 μ m. The TiN-cracks are blunted out before the conditions for cleavage are attained. This can be ascribed to influence of a large plastic zone which is produced ahead of the ductile crack. In addition to being more resistant to brittle crack propagation across particle/matrix interface, the steels with AF structure show the susceptibility to cracks being arrested at the grain boundaries presumably AF plate boundaries. This feature is observed only in steels with AF and not with BS structure, providing thus additional burriers to crack propagation in the former.

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

Thursday AM Room: 7B
March 4, 1999 Location: Convention Center

Session Chairs: John L. Lombardi, Advanced Ceramic Research, Tuscon, AZ 85706-5013 USA; John E. Smugeresky, Sandia National Laboratory, Livermore, CA 94551 USA

8:30 AM
BALLISTIC TESTING OF LASER FREE-FORM FABRICATED Ti-6Al-4V: *William Herman*[1]; Eric Whitney[2]; [1]General Dynamics, Land Systems Division, 6000 East Seventeen Mile Rd., Sterling Heights, MI 48313-4500 USA; [2]Pennsylvania State University, Applied Research Laboratory, P.O. Box 30, State College, PA 16804 USA

Laser free form fabrication is a process to manufacture complex shapes without the use of molds or dies. The process utilizes a laser to melt and fuse powder or wire along a predefined computer controlled path. The fabrication of structural shapes differs from prototyping in that the material produced for structural applications must, naturally, be fit for use. One application for laser free form fabricated Ti-6Al-4V shapes is the manufacture of large, lightweight components for armored vehicles. This study compares the ballistic properties of Ti-6Al-4V material produced in a high power (14 kW CO2) laser free form process to conventionally prepared wrought and cast Ti-6Al-4V. Tensile and chemical tests were also prepared and compared to previously laser fabricated Ti-6Al-4V. Material was laser fabricated to meet the chemistry of MIL-T-9046 using gas atomized pre-alloyed powder. Ballistic testing using 20mm Fragment Simulated Projectiles and 0.50 caliber armor piecing rounds was conducted in accordance with MIL-A-46077.

8:50 AM
FABRICATION OF TOOL STEEL INSERTS FROM SFF PATTERNS USING THE RSP TOOLING PROCESS: *Kevin M. McHugh*[1]; [1]INEEL/Lockheed Martin, P.O. Box 1625, Idaho Falls, ID 83415-2050 USA

Rapid Solidification Process (RSP) Tooling is an alternative method for making tooling inserts which shows promise for reducing fabrication time and cost compared to conventional approaches. The approach combines rapid solidification of metals with net-shape materials processing in a single step. A molten tool forming alloy is atomized by the action of a high velocity gas jet to form very fine droplets that are entrained by the jet and deposited onto an SFF or other pattern. As the deposit builds up, it faithfully replicates the pattern's shape, surface texture and surface detail. Production rates are high, on the order of 500 lbs./hr using a bench scale system, allowing the inserts to be spray formed in minutes. This paper summarizes recent advances in processing and describes how material and microstructural properties transform during solidification and subsequent heat treatments.

9:10 AM

ESTIMATION OF LASER POWER FOR FREE-FORM FABRICATION: *Eric Whitney*[1]; [1]Pennsylvania State University, Applied Research Laboratory, P.O. Box 30, State College, PA 16804 USA

An energy balance approach for the estimation of the laser power needed to perform a laser free-form fabrication process is discussed. The approach takes into account the melting of the filler metal and a small portion of the substrate. The technique employed utilizes a modification of the energy balance approach taken for laser welding. Although a strict energy balance does not take into consideration other process requirements, such complete fusion between beads and layers and other metallurgical requirements, a simple set of rules can be used to impose practical limits on the energy balance. The approach is applied to commercially pure titanium and Ti-6Al-4V alloy.

9:30 AM

LASER FREE-FORM FABRICATION OF NICKEL-ALUMINUM-BRONZE: *Eric Whitney*[1]; Kenneth C. Meinert[1]; [1]Pennsylvania State University, Applied Research Laboratory, P.O. Box 30, State College, PA 16804 USA

The fabrication of the large structural shapes using laser free form fabrication techniques is of great practical interest because it offers the potential of significantly reducing costs, particularly for low volume production runs. Implementing laser free from fabrication technology can also reduce costs by eliminating the need to inventory a large quantity of specific tooling. This benefit is especially true for the procurement of replacement parts that are no longer manufactured as part of new production. Another benefit of laser free from fabrication process is the capability of making functionally graded compositions. In this paper the results of feasibility study on laser free from fabrication of a nickel-aluminum-bronze (NAB) alloy. Laser processing was performed using a 14 kW CO2 laser and a specially constructed environmental chamber. The environmental chamber was purged with oxygen such that the oxygen level in the chamber was less than 200 ppm. Chemical analysis showed that chemical composition between the precursor powder and the deposit was essentially unchanged by the laser deposition process. Mechanical properties were also tested and shown to be comparable to conventionally cast NAB. Finally, a functionally graded shape was made where the composition was initially that of Alloy 625 and graded to NAB.

9:50 AM

LASER-DEPOSITED HIGH TEMPERATURE MATERIALS: *Xiao-Dong Zhang*[1]; Richard Grylls[1]; Hamish Fraser[1]; [1]The Ohio State University, Materials Science and Engineering, 2041 College Rd., Columbus, OH 43210 USA

The objective of this work is to characterize the microstructure of high temperature materials produced by Laser Engineered Net Shaping (LENS®). LENS is a laser direct metal deposition process that combines laser cladding technologies with advanced rapid prototyping methods with the capability to directly manufacture complex three-dimensional components. Various alloys have been deposited including TiAl and Ni-based superalloys. Components were generated using a CW Nd: YAG laser operated at about 150-200 watts. Characterization was conducted using optical microscopy, SEM and TEM. Different microstructure can be obtained depended on the processing parameters (laser scan speed, powder feed rate and pressure, substrate subtract materials and post-heat- treatment). A number of high temperature metastable phases have been retained at room temperature in several of these alloys. By careful control of post- heat- treatment, optimum microstructures and mechanical properties may be obtained. This work will compare the microstructures of these laser-deposited materials with those typically seen in materials produced by more conventional means. The significance of the LENS® technique will be discussed in terms of near net-shape manufacture, microstructural control and potential applications.

10:10 AM BREAK

10:25 AM

ISSUES ASSOCIATED WITH THE DEVELOPMENT OF A WATER SOLUBLE SUPPORT FOR USE IN FREEFORMING: *John L. Lombardi*[1]; Gregory G. Artz[1]; Ranji Vaidyanathan[1]; [1]Advanced Ceramics Research, Inc., 3922 East Hemisphere Loop, Tuscon, AZ 85706-5013 USA

Freeforming are promising techniques for fabricating complex shaped prototype and low volume production components. Unfortunately many prototypes have complicated geometries (i.e. overhangs or internal features) such that they are not easily fabricated by these techniques without the assistance of a fugitive material to support the freeformed layers. Conventional freeforming techniques utilize a fugitive support material which must be removed from the completed part using either mechanical or thermal pyrolysis means. This paper discusses the development and characterization of a fugitive support which is soluble in aqueous solution.

10:45 AM INVITED PAPER

HIGH TEMPERATURE FILTERS MADE BY CERAPRINT♦: *Mark V. Parish*[1]; Andrew B. Jeffrey[1]; [1]Specific Surface Corporation, 101 Constitution Blvd., Franklin, MA 02038 USA

Ceramic and metal filters made using a manufacturing process called CeraPrint♦ will be discussed. CeraPrint♦ is based on Three Dimensional Printing♦ technology developed at MIT. Filters are made with controlled macro- and micro- structures using this manufacturing process that uses advanced liquid jetting technology and readily available powders. CeraPrint♦ allows a high degree of design and materials flexibility that is necessary in order for ceramic and metals to compete in the filtration market. Complex filter designs can be made without tooling or molds in a competitive manner, allowing for high surface area designs with uniform and controlled porosity. The process is scalable to virtually any size. Our CleanStac♦ filters, for example, have been designed for conventional filtration baghouses where operating temperatures of up to 600ϒC are desired. Operation in corrosive gas streams is also achieved with CleanStac♦. The presentation will include discussion of operations of CleanStac♦ filters in COHPAC I an II power generation pilot plants . In COHPAC I, CleanStac♦ rigid ceramic filters operated for 2,000 hours under a variety of conditions to test baghouse applications. Results have shown very good performance with low pressure drop and high filtration efficiency. CleanStac♦ filters were shown to be cleaned effectively using existing pulse jet technology.

11:15 AM

FUNCTIONALLY GRADIENT CERAMIC COMPOSITES VIA FUSED DEPOSITION PROCESS: *Raj Atisivan*[1]; Ashwin Hattiagadi[1]; M. Rubiela Diaz[1]; Susmita Bose[1]; [1]Washington State University, Amit Bandyopadhyad School of Mechanical and Materials Engineering, Pullman, WV 99164-2920 USA

Functionally gradient materials (FGM) show a variety of properties from one end of the material to the other end due to its compositional variation. Fused deposition modeling (FDM) process has been utilized to process functionally gradient ceramic-polymer and metal-ceramic composites. Porous ceramic preforms with a gradient in porosity from one end to the other are fabricated via indirect freeform fabrication route. The porous ceramic preforms are then infiltrated with polymers and metals to form a ceramic-polymer and metal-ceramic composites. Room temperature mechanical properties of these composites are tested with respect to the volume fraction ceramics content. In this presentation, functionally gradient alumina, mullite and silica ceramic composites will be discussed.

11:35 AM

EXTRUSION FREEFORM FABRICATION OF SILICON NITRIDE PARTS: *Ranji Vaidyanathan*[1]; John L. Lombardi[1]; Blake Tennison[1]; Sridhar Kasichainula[2]; P. Calvert[2]; [1]Advanced Ceramics Research, Inc., Tuscon, AZ 85706 USA; [2]University of Arizona, Arizona Materials Laboratories, Tuscon, AZ 85713 USA

Extrusion Freeforming (EFF) and Fused Deposition Modeling (FDM) processes are established freeforming techniques capable of fabricating complex shaped ceramic prototypes by the sequential deposition and solidification of green ceramic feedstock, layer by layer until the final part results. This paper will detail the development and characterization of a complicated ceramic prototype part using the EFF process and ACR's patented high-pressure extrusion head technology. Development of a suitable ceramic filled binder system for the high-pressure extrusion

head will be presented. Optimization of the binder burnout and sintering cycles, and characterization of the parts will also be discussed.

SYNTHESIS OF LIGHTWEIGHT METALS III: Magnesium

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

Thursday AM Room: 10
March 4, 1999 Location: Convention Center

Session Chairs: P. G. McCormick, University of Western Australia, Research Centre for Adv. Min. and Mats. Proc., Nedlands, Western Australia 6907; D. Eliezer, Ben Gurion University, Dept. of Mats. Eng., Beer-Sheva 84105 Israel

8:30 AM INVITED PAPER

OVERVIEW OF MAGNESIUM - PART I: *Dan Eliezer*[1]; Eli Aghion[2]; F. H. (Sam) Froes[3]; [1]Ben-Gurion University of the Negev, Dept. of Mats. Eng., P.O. Box 653, Beer-Sheva 84105 Israel; [2]Dead Sea Magnesium Works, Ltd., Potash House, P.O. Box 75, Beer Sheva 84100 Israel; [3]University of Idaho, IMAP, Mines Bldg., Rm. 321, Moscow, ID 83844-3026 USA

The very low density and excellent castability of magnesium is leading to increased use in various applications, especially in automobiles, despite poor galvanic corrosion resistance and a higher cost than aluminum. Further expansion of the magnesium market should come from reduced cost, and increased design base, a better understanding of the scientific underpinning of magnesium alloys, improved protection systems, and the development of cost-affordable cast and wrought products. Magnesium is considered as an environmentally friendly material that can be easily recycled. The potential use of magnesium is strongly related to environmental conservation awareness.

8:50 AM INVITED PAPER

OVERVIEW OF MAGNESIUM - PART II: *Dan Eliezer*[1]; Eli Aghion[2]; F. H. (Sam) Froes[3]; [1]Ben-Gurion University of the Negev, Dept. of Mats. Eng., P.O. Box 653, Beer-Sheva 84105 Israel; [2]Dead Sea Magnesium Works, Ltd., Potash House, P.O. Box 75, Beer Sheva 84100 Israel; [3]University of Idaho, IMAP, Mines Bldg., Rm. 321, Moscow, ID 83844-3026 USA

The very low density and excellent castability of magnesium is leading to increased use in various applications, especially in automobiles, despite poor galvanic corrosion resistance and a higher cost than aluminum. Further expansion of the magnesium market should come from reduced cost, and increased design base, a better understanding of the scientific underpinning of magnesium alloys, improved protection systems, and the development of cost-affordable cast and wrought products. Magnesium is considered as an environmentally friendly material that can be easily recycled. The potential use of magnesium is strongly related to environmental conservation awareness.

9:10 AM

SYNTHESIS OF Mg2Si BY MECHANICAL ALLOYING: *A. Alvarez*[1]; E.G. Baburaj[1]; Swati Ghosh[1]; F. H. (Sam) Froes[1]; [1]University of Idaho, IMAP, Mines Bldg., Rm. 321, Moscow, ID 83844-3026 USA

Magnesium alloys containing Mg_2Si particles have the potential for applications as light weight alloys for relatively higher temperatures compared to other Mg alloys, because of their high melting point, low density, high hardness and low coefficient of thermal expansion. In the present work a combination of mechanical alloying and heat treatments has been employed to synthesize Mg_2Si. During mechanical alloying, powder particles fracture and re-weld resulting in the formation of lamellar structure. With increasing milling time lamellae thickness decreases, while defect concentration within the lamellar structure increases. Due to the large concentration of defects at the inter-lamellar boundaries diffusion becomes easier around these defect concentrations and hence continued milling results in the formation of Mg_2Si intermetallic compound. A set of experiments has also been carried out to ascertain the inter-dependence of milling time and heat treatments on the formation of the intermetallic. The compound formation temperature has been found to decrease with increase in milling time.

9:30 AM BREAK

9:45 AM

THE ROLE OF SECOND PHASES IS THE CORROSION MECHANISM OF MAGNESIUM AZ91 ALLOY: *P. Uzan*[1]; D. Eliezer[1]; E. Aghion[2]; [1]Ben-Gurion University of the Negev, Dept. of Mats. Eng., P.O. Box 653, Beer-Sheva 84105 Israel; [2]Dead Sea Magnesium, Ltd., Magnesium Research Division, P.O. Box 75, Beer-Sheva, 84100 Israel

Due to the light weight of magnesium alloys they have been continuously considered as structural materials in the transportation and electric industries. The most common Mg alloy in use is the AZ91D which has adequate corrosion resistance. However, one of the major causes for corrosion deterioration is the presence of impurities, non-metallic inclusions and intermetallic phases. Some of these phases may be more cathodic comparing to the Mg matrix and hence it is important to understand their effect on the corrosion mechanism of the magnesium alloys. The present study aims to evaluate the corrosion behavior of AZ91 alloy in view of the above phases. This paper will emphasize the effect of the second phases on the corrosion mechanism with the focus on the effect of the β ($Mg_{17}Al_{12}$) phase that will be discussed in detail. In order to understand the effect of the β phase, the corrosion performance of Mg AZ91 alloy in as cast (F), homogenized (T4) and artificially-aged (T6) conditions were evaluated under immersion test conditions and potentiodynamic polarization analysis in NaCl and $Mg(OH)_2$ electrolyte.

10:05 AM

MICROSTRUCTURE REFINEMENT OF Al-Mg-Si CAST INTERMETALLIC ALLOYS: *M. Bamberger*[1]; [1]Technion, Dept. of Mats. Eng., Israel Institute of Technology, Haifa 32000 Israel

Nano-crystalline powders added to molten metallic-alloys can modify the as-cast microstructure by inoculation, or by restricting grain growth of the primarily solidified intermetallic phase. The modification mechanism of the primarily solidified Mg_2Si, formed during the solidification of Mg_2Si- 50%wtAl intermetallic alloys, by nano-crystalline TiCN was investigated. Up to 10%wt of nano-crystalline TiCN powder (typical mean particle size 45-70nm) was added to molten Mg-Si-Al alloys. The microstructure of the modified and un-modified alloys was investigated using SEM/EDS, TEM/EDS, X-ray diffraction and optical microscopy. In addition, "model experiments", in which Mg-alloys were infiltrated into porous TiCN, were used to investigate their solidification sequence. Inoculation with TiCN leads to a decrease in the grain size of the primarily solidified Mg_2Si from 25-80μm to 0.1-0.8μm. The microhardness of the regions containing the ultrafine microstructure was 314-428Hv, as compared to 129-142Hv obtained from the unmodified structure. No cracks were detected after microhardness (1000gr) tests in modified regions, whereas cracks were found in the un-modified microstructure even after loading at only 100gr. Microstructural analysis revealed rejection of the TiCN from the intermetallic phase, which in turn limits growth of the Mg_2Si during solidification, and hence a fine microstructure is obtained by restricting grain growth mechanism.

10:25 AM

STRUCTURAL STABILITY AND CREEP PROPERTIES OF AZ91:

M. Regev[1]; A. Rosen[1]; M. Bamberger[1]; [1]Technion, Dept. of Mats. Eng., Israel Institute of Technology, Haifa 32000 Israel

Creep properties of AZ91D magnesium alloy (9%Al - 1%Zn) ingot castings having different microstructure were investigated in this research work within the temperature range of 120-180ϒC. The specimens of the ingot (taken from the equi-axed grains zone) are characterized by a relatively coarse grain size (~300μm) of magnesium matrix containing aluminum in solid solution and β($Mg_{17}Al_{12}$) precipitates. Aging study of the ingot casting, performed at the temperatures of 120ϒC and 180ϒC, yielded that the microstructure is thermally unstable at these temperatures. Aged specimens were investigated by optical and scanning electron microscopes and sub micron precipitates of β($Mg_{17}Al_{12}$) were detected near the matrix grain boundaries. Creep tests were performed on ingot specimens under three conditions: in the as cast condition, after solution heat treatment and after aging heat treatment.