TMS

Become A TMS Member

TMS derives its strength from its members, who take a hands-on approach to shaping the policy, programming, and publications of the society. Guided by these volunteers, TMS serves all segments of its professional community by:

FACILITATING NETWORKING:

By sponsoring numerous annual meetings and specialty conferences, TMS maximizes the opportunities for professionals from industries, universities, and government agencies worldwide to meet face to face and exchange technical ideas and experience, offer customer/client insights, find a mentor and/or serve as one, and just plain chat with peers and colleagues.

PRODUCING JOM AND OTHER PUBLICATIONS:

Every TMS member receives a complimentary subscription to JOM. Formerly Journal of Metals, this highly respected monthly journal, explores traditional, innovative, and revolutionary issues in the minerals, metals, and materials fields. Designed to be of maximum and immediate benefit to readers throughout the world, JOM is on-line before the print version is mailed.

TMS also publishes three other journals (*Journal of Electronic Materials* and *Metallurgical and Materials Transactions A and B*), numerous conference proceedings volumes and textbooks, and videos designed to give materials scientists and engineers the latest information on scientific and applied advances in areas as diverse as electronic materials, automotive manufacture, and extractive metallurgy.

PROMOTING LIFE-LONG LEARNING:

TMS is dedicated to the education of the materials science and engineering professional as well as to cultivating an interest in the field by young people.

For the practicing professional, TMS and its five technical divisions sponsor continuing education courses, primarily technical but also nontechnical, to promote the education and development of current and future professionals.

For student members, TMS participates on both the Accreditation Board for Engineering & Technology (ABET) and the National Council of Examiners for Engineering and Surveying (NCEES) to help, respectively, maintain the highest possible standards in the accreditation of metals and materials programs in academia and in the registration of professional engineers.

—All individuals registering for the 131st Annual Meeting & Exhibition at the non-member fee will automatically receive a one-year complimentary introductory membership for 2002. Your membership will be activated upon completion of your registration form, membership application, and payment of the non-member registration fee. You will receive a membership card and new member packet immediately after the meeting.

• Members from 77 countries and six of the world's seven continents.

• All new members will begin receiving a monthly subscription to JOM.

• New members will also be able to continue networking with a prestigious membership at future TMS meetings that fit their area of interest at a discounted member fee.

• Additional benefits include access to, and inclusion in the TMS Membership Directory on TMS OnLine at www.tms.org., professional development and continuing education opportunities, and group insurance programs. See the membership page on TMS OnLine for a complete list of membership benefits.

• Please direct any questions regarding your complimentary membership to the TMS Member Services Department via email to castello@tms.org or via phone to Margie Castello (724) 776-9000 Ext. 241.

TMS THE MINERALS, METALS & MATERIALS SOCIETY

PROMOTING THE GLOBAL SCIENCE AND ENGINEERING PROFESSIONS CONCERNED WITH MINERALS, METALS, AND MATERIALS

184 THORN HILL ROAD
WARRENDALE, PA 15086-7514
USA

TELEPHONE: (724) **776-9000**
(800) **966-4867**
FAX: (724) **776-3770**
WEB: **www.tms.org**

THE VISION OF TMS IS TO BE THE PROFESSIONAL SOCIETY OF CHOICE FOR THE WORLDWIDE MINERALS, METALS AND MATERIALS COMMUNITY.

GREAT MEMBER BENEFITS

- Five distinct technical divisions which are composed of 52 separate, highly specialized committees
- Periodicals: JOM, Metallurgical and Materials Transactions A and B, Journal of Electronic Materials
- Conference Proceedings, Monographs, and Textbooks
- TMS OnLine & the TMS Document Ordering Center
- TMS Conferences: TMS Annual Meeting & Exhibition, TMS Fall Meeting, TMS Fall Meeting for Extraction & Processing, Electronic Materials Conference, Specialty Conferences
- Professional Development and Continuing Education Opportunities
- Professional Registration
- TMS Young Leaders
- TMS Resume Referral Service
- TMS Gold or Platinum MasterCard
- Group Insurance
- TMS Membership Directory
- TMS Speakers Directory
- International Healthcare Plan
- Hertz Car Rental Discounts
- Auto and Homeowners Program
- PROinsure Program
  A Professional Liability/Errors and Omissions Program
- PRObop Program
  A Professional Business Owners Package Program
- Member Benefits Program
  Receive a 20% Rebate Buying or Selling Your Home
- Nelson Financial Services Program
- WAAIME Auxiliary Activities

ADMISSION REQUIREMENTS

FULL MEMBER

A candidate for election as full member shall be a person of integrity in activities associated with minerals extraction, processing, fabrication, or with materials applications. A candidate shall hold: (a) A baccalaureate degree in metallurgy, metallurgical engineering, materials science, or materials engineering, and at least 3 years' professional experience. (b) A baccalaureate degree in science or engineering in a discipline other than identified and at least 5 years' professional experience. (c) A baccalaureate degree from a recognized university in a discipline other than (a) or (b) and whose main activities lie in, but are not limited to, the development, management, administration, welfare, sales, or services to the minerals, metals and materials industries, with at least 7 years' experience. A credit in experience of one year for a masters degree or two years for a doctoral degree shall be granted.

Annual dues: $90.00

ASSOCIATE MEMBER

A candidate for associate member shall be a person of integrity who, while not possessing the academic or technical experience of a member, is active in fields that are sufficiently related to the advancement of, or service to, the minerals, metals or materials extraction, processing, or applications industry.

Annual dues: $90.00

The Minerals, Metals & Materials Society is a member society of the American Institute of Mining, Metallurgical and Petroleum Engineers, Inc.

LIFE MEMBER

A candidate for election as life member shall be a person who qualifies as a full member or associate member and desires to only pay dues once.

Dues: $1,350.00

Pay dues once, effective for lifetime regardless of dues increase(s).

REINSTATEMENT

Those members who may have let their dues payment lapse may reinstate in the same grade as when they left by submitting a new application and paying a reinstatement fee of $10.00 plus current dues. If original election year is desired, back dues must be paid to date (half the annual dues fee for each year of lapsed membership); otherwise, election year will be year of reinstatement.

The TMS membership year runs from January 1–December 31. Applications received January 1–September 30 will be processed for the current calendar year.

Applications received after September 30 will be processed for the remainder of the current calendar year and the entire following year. Membership benefits commence upon processing; subscriptions commence January–December of the following year.

Two weeks required for processing of complete applications submitted with full payment. Incomplete applications will not be processed. Allow eight to ten weeks for subscriptions to start.

MEMBERSHIP APPLICATION

PLEASE TYPE OR PRINT

❒ Mr. ❒ Mrs. ❒ Ms.
❒ Dr. ❒ Professor

SEND MAIL TO:
- ❒ Business Address
- ❒ Home Address

TECHNICAL DIVISION SELECTION:
- ❒ Electronic, Magnetic, & Photonic Materials Division
- ❒ Extraction & Processing Division
- ❒ Light Metals Division
- ❒ Materials Processing & Manufacturing Division
- ❒ Structural Materials Divison

THROUGH WHAT MEANS WERE YOU ENCOURAGED TO JOIN TMS?
- ❒ TMS Annual Conference
- ❒ TMS Fall Conference
- ❒ Specialty Conference
- ❒ Exhibitor
- ❒ TMS Staffed Booth
- ❒ JOM
- ❒ MET TRANS, JEM, Etc.
- ❒ Publications Catalog
- ❒ TMS Mailed Brochure
- ❒ Non-TMS Advertisement
- ❒ Continuing Education
- ❒ TMS OnLine/Web
- ❒ Colleague
- ❒ Other _______________

BIRTHDATE:

________/________/________

Members automatically receive a monthly print subscription to JOM.

If you prefer to receive your copy only electronically, please check here. ❒

If you prefer to receive your subscription in both print and electronic formats, please check here. ❒
(You must include $8 extra charge.)

If you would like additional information about member subscriptions and discounts to JOM, Journal of Electronic Materials, or Metallurgical and Materials Transactions A and B, please check here. ❒

FOR OFFICE USE ONLY

ID

BIRTH

ELECTED

TYPE

CATEGORY

SECTION

APPROVED

NAME: ______________________________________
LAST FIRST MIDDLE INITIAL

TITLE: ______________________________________

COMPANY OR ORGANIZATION: ______________________________________

BUSINESS: ______________________________________
STREET OR P. O. BOX CITY STATE 9 DIGIT ZIP/POSTAL CODE COUNTRY

____
PHONE FAX TOLL FREE # E-MAIL WEB ADDRESS

HOME: ______________________________________
STREET OR P. O. BOX CITY STATE 9 DIGIT ZIP/POSTAL CODE COUNTRY

____
PHONE FAX E-MAIL

____
MONTH DAY YEAR

WHAT IS THE PRIMARY ACTIVITY OF YOUR PLACE OF EMPLOYMENT? (check one)
- ❒ Commercial Laboratory
- ❒ Government/Nonprofit Laboratory
- ❒ Engineered Materials Producer
- ❒ Manufacturer of Parts/Components
- ❒ Manufacturer of Finished Products (OEMs)
- ❒ Primary Metals Producer
- ❒ Secondary Metals Producer
- ❒ Producer/Processor of Materials
- ❒ Educational
- ❒ Engineering or Consulting Firm
- ❒ Other ____________________

WHAT BEST DESCRIBES YOUR PRIMARY JOB FUNCTION? (check one)
- ❒ Applications/Product Development
- ❒ Basic Research
- ❒ Product Engineering and Design
- ❒ Technical/Lab Management
- ❒ Process Engineering
- ❒ Metallurgical Materials Selection
- ❒ Corporate Management
- ❒ R & D Engineer
- ❒ R & D Scientist
- ❒ R & D Management
- ❒ Manuf./Production Management
- ❒ Quality Engineering
- ❒ Marketing or Sales
- ❒ Other ____________________
- ❒ Consultant
- ❒ Educator
- ❒ Student

OTHER SOCIETY AFFILIATIONS: ______________________________________

EDUCATION TO DATE:

	Name of School	Dates Attended Month/Year–Month/Year	Major Subject/ Engineering Field	Degree Received or Expected Graduation Date: Month/Year
B.S. ❒				
M.S. ❒				
Ph.D. ❒				

REGISTERED PROFESSIONAL ENGINEER? ❒ Yes ❒ No STATE: __________ YEAR OF REGISTRATION: __________

RECORD OF EXPERIENCE:
(List most recent record of employment. If you do not possess a qualifying degree, please include your last seven years of experience.)

From: __________ Title: ______________________________

Company: ______________________________

To: __________ Nature of Company's Business: ______________________________

Total Time with Company: ______________________________

Engineering Responsibilities: ______________________________

TO APPLICANT

If you have been encouraged to submit this application by a current member of TMS, please complete the following information:

Member's Name ______________________________ Member # ______________

I agree, if elected, to accept election, and to abide by the TMS bylaws.

Signature ______________________________ Date ______________

PREPAYMENT IS REQUIRED (checks should be made payable to TMS in U.S. dollars drawn on a U.S. bank)
- ❒ Check enclosed
- ❒ Bill my credit card: (check one)
  - ❒ American Express ❒ VISA ❒ MasterCard ❒ Diners Club

Credit Card # ______________________________ Expiration Date ______________

Cardholders Name ______________________________

Signature ______________________________

COMPLETE APPLICATION AND MAIL WITH PAYMENT TO: **184 Thorn Hill Road, Warrendale, PA 15086-7514**
Phone: 800-966-4867 or 724-776-9000 • Fax: 724-776-3770

WEB	FAX	MAIL
Take advantage of the convenience of on-line pre-registration via the TMS website: **http://www.tms.org** Web registration requires credit card payment.	Fax this form to TMS Meeting Services **USA 724-776-3770** Fax registration requires credit card payment.	**Return this form with payment to** Meeting Services TMS 184 Thorn Hill Road Warrendale, PA 15086

TMS2002
131st Annual Meeting & Exhibition

AM02-PDF

Advance Registration Deadline: January 28, 2002
Payment must accompany form.
Forms received past this date will be processed at the on-site fee.
INSTRUCTIONS: Check your selections and fill in the necessary information. *Please print or type.*

Member of: ☐ TMS ☐ ISS ☐ SME ☐ SPE Member Number: ____________________

This address is: ☐ Business ☐ Home Employer/Affiliation: ____________________

☐ Dr. ☐ Prof. ☐ Mr. ☐ Mrs. ☐ Ms. Title: ____________________

____________________ LAST NAME ____________________ FIRST NAME ____________________ MIDDLE INITIAL

Address: ____________________

City: ____________________ State/Province: __________ Zip/Postal Code: __________ Country __________

Telephone: ____________________ (COUNTRY AREA/CITY LOCAL NUMBER) Fax: ____________________ (COUNTRY AREA/CITY LOCAL NUMBER)

E-Mail Address: ____________________ Guest/Spouse Name: ____________________
GUESTS DO NOT RECEIVE ADMISSION TO TECHNICAL SESSIONS.

Registration Fees:

	Advance Fees (until 1/28/02)	On-Site Fees (after 1/28/02)
☐ Member	$395 M	$495 ML
☐ Non-Member Author	$395 NMA	$495 NMAL
☐ Non-Member *	$520 NM	$620 NML
☐ Student Member ##	$0 STU	$0 STUL
☐ Student Non-Member ## *	$25 STUN	$25 STUNL
☐ TMS Retired Member	$220 RM	$220 RML
☐ Exhibit Booth Personnel	$0 E	$0 EL
☐ Exhibit Only	$35 EO	$35 EOL

* Includes TMS membership for 2002
Students must attach a copy of their school's student identification card.

Publication Orders:

ALL pre-ordered books not indicated for shipment MUST be picked up at the Publications Sales area in the convention center.

Qty.	Order Number and Title	Book Price	Shipping*	Total
___	#514X CALPHAD and Alloy Thermodynamics	$72	+_____	=_____
___	#5158 Creep Deformation: Fundamentals and Applications	$105	+_____	=_____
___	#5166 EPD Congress 2002	$96	+_____	=_____
___	#5182 High-Cycle Fatigue, the David L. Davidson symposium	$110	+_____	=_____
___	#5190 Light Metals 2002 (Book and CD-ROM set)	$158	+_____	=_____
___	#5247 Magnesium Technology 2002 (Book and CD-ROM set)	$111	+_____	=_____
___	#5204 Science and Technology of Interfaces, International Symposium in Honor of Dr. Bhakta Rath (PDF)	$122	+_____	=_____
___	#5255 Sulfide Smelting 2002	$70	+_____	=_____
___	#5212 Surface Engineering: Science and Technology II (PDF)	$111	+_____	=_____
___	#5220 High-Performance Metallic Mat'ls for Cost-Sensitive Applications (PDF)	$117	+_____	=_____
___	#5239 Ultrafine Grained Materials II	$125	+_____	=_____
___	#5131 Computational Modeling of Materials Minerals, and Metals Processing	$129	+_____	=_____

* Shipping: in the United States–$10 per item • all other countries–$20 per item

Tutorial Luncheon Lecture Tickets

Optional Box Lunches	Fee	No.	Total
Monday 2/18/02 (sponsored by Young Leaders)			
Young Leaders Tutorial Box Lunch	$25	_____	$______

Refund policy: Written requests must be mailed to TMS, post-marked no later than January 28, 2002. A $50 processing fee will be charged for all meeting registration cancellations in addition to all short course registrations cancellations.

Continuing Education Short Courses:

	Advance Fees (until 1/28/02)	On-Site Fees (after 1/28/02)
Aluminum Smelter Cell Dynamics		
☐ Member	$645	$695
☐ Non-Member	$735	$785
Texture and Anistrophy for the Materials Professional		
☐ Member	$395	$475
☐ Non-Member	$445	$525
Computational Modeling Techniques and Applications for Materials Processing		
☐ Member	$395	$475
☐ Non-Member	$445	$525

Social Function Tickets:

	Fee	No.	Total
Monday 2/18/02			
Bhakta Rath Honorary Dinner	$60	_____	$______ RD
Charles McMahon Honorary Dinner	$60	_____	$______ MD
David L. Davidson Honorary Dinner	$35*	_____	$______ DD
* A portion of each ticket is being subsidized by the organizing committee			
Tuesday 2/19/02			
TMS Banquet	$60	_____	$______ AD
Tables of 8	$480	_____	$______ AD8
Table Sign to Read ____________________			
Extraction & Processing Division Luncheon	$30	_____	$______ EP
Tables of 8	$240	_____	$______ EP8
Table Sign to Read ____________________			
Wednesday 2/20/02			
Light Metals Division Luncheon	$30	_____	$______ LM
Tables of 8	$240	_____	$______ LM8
Table Sign to Read ____________________			

Plant Tour:

Thursday 2/21/02	Fee	No.	Total
Boeing 747/767/777	$39	_____	$______BT

2002 Membership Dues—for current TMS members only:

☐ Full Member	$90 FM
☐ Junior Member	$55 JM
☐ ASM/TMS Joint Student Member	$25 ST

TOTAL FEES PAID .... $____________

Payment enclosed:

☐ Check, Bank Draft, Money Order

Make checks payable to TMS. Payment shall be made in US dollars drawn on a US bank.

☐ Credit Card Expiration Date: ____________________

Card No.: ____________________

☐ Visa ☐ MasterCard ☐ Diners Club ☐ American Express

Cardholder Name: ____________________

Signature: ____________________

TMS2002

131st Annual Meeting & Exhibition

February 17-21, 2002 • Seattle, Washington, USA

Making your reservation is easier than ever through Travel Planners' real-time Internet reservation system! Just log on to www.tms.org, and follow the link to Travel Planners. You will be able to view actual availability, learn about your hotel's features and services, and obtain local city and sightseeing information. Most importantly, you will receive instant confirmation of your reservation!

Or, mail or fax this housing form to:
Travel Planners, Inc., 381 Park Ave. South,New York, NY 10016
FAX: 212-779-6128 • PHONE: 800-221-3531, ext. 1 (in 212, 718, 516, 914, 631 or international call 212-532-1660, ext. 1)
(CHOOSE ONLY ONE OPTION)

Reservations must be received at Travel Planners by: January 18, 2002

Arrival Date ____________ Departure Date ____________

Last Name ____________ First Name ____________ MI ________

Company ____________

Street Address ____________

City ____________ State/Country ____________ Zip/Postal Code ________

Daytime Phone ____________ Fax ____________

Additional Room Occupants ____________

E-mail ____________ (confirmation will be sent via e-mail if address is provided)

Non-Smoking Room Requested ____________ Special Needs ____________

 # after hotel correspondes with map below.

HEADQUARTERS
Sheraton Hotel • 1
$175/single • $175/double

W Hotel Seattle • 7
$179/single • $199/double

Renaissance Madison • 5
$149/single • $149/double

West Coast/Grand • 8
$135/single • $135/double

Hilton Seattle • 3
$140/single • $140/double

Mayflower Park Hotel • 4
$140/single • $140/double

West Coast/Roosevelt • 9
$132/single • $132/double

Westin Seattle • 11
$165/single • $165/double

Crowne Plaza Seattle • 2
$134/single • $134/double

Summerfield Suites Wyndham • 6
$119/single • $129/double

West Coast/Vance • 10
$125/single • $125/double

Indicate 1st, 2nd, & 3rd hotel choice:

1. ____________
2. ____________
3. ____________

Type of Accomodations: (check one)
☐ Single 1 person/1bed ☐ Double 2 people/1bed ☐ Twin 2 people/2 beds
☐ Triple 3 people/2 beds ☐ Quad 4 people/2 beds

If all three (3) requested hotels are unavailable, please process this reservation according to: (check one) ☐ ROOM RATE ☐ LOCATION

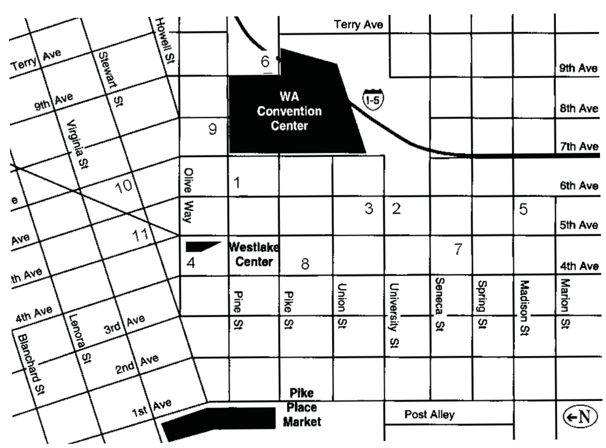
TMS has contracted a block of rooms at the headquarters hotel, Sheraton Seattle Hotel & Towers, along with each of the hotels, and therefore has assumed a financial liability for any and all rooms in that block that are not reserved. You are strongly encouraged to reserve your room(s) at the hotels listed to limit our financial liability. Please help TMS achieve overall success with the 131st TMS Annual Meeting & Exhibition by making your reservation at one of the listed hotels prior to the advance housing deadline. Thank you.

Confirmations: Confirmation will be e-mailed, faxed or mailed to you from Travel Planners, Inc. once your reservation has been secured with a deposit. You will not receive a confirmation from your hotel. If you do not receive a confirmation within 7 days, please call Travel Planners, Inc.

Changes/Cancellations: All changes and cancellations in hotel reservations must be made with Travel Planners, Inc. up until 3 business days prior to arrival and are subject to the individual hotel's cancellation policies. Cancellations and changes within 3 days of arrival MUST be made with your hotel directly. Many hotels are now imposing fees for early departure. This rate is set by each hotel and may vary accordingly. Please reconfirm your departure date at the time of check-in.

Reservations/Deposits: All reservations are being coordinated by Travel Planners, Inc. Arrangements for housing must be made through Travel Planners, Inc. and NOT with the hotel directly. Reservations via Internet, phone or fax will be accepted with a major credit card only. Housing forms and written requests will be accepted with a major credit card or deposit of one night's room and tax payable to Travel Planners, Inc. Check must be drawn in US funds on a US bank. No wire transfers will be accepted. Deposit policies are set by each hotel, and are outlined on your hotel confirmation.

Please read all hotel information prior to completing and submitting this form to Travel Planners, Inc. Keep a copy of this form. Use one form per room required. Make additional copies if needed.



Payment enclosed: ☐ Check ☐ American Express ☐ MasterCard ☐ VISA ☐ Discover ☐ Diners

Account Number ____________ Expiration Date ____________

Card Holder Name ____________ Authorized Signature ____________

TMS2002

131st Annual Meeting & Exhibition

February 17-21, 2002 • Seattle, Washington, USA

Convention Services Northwest has arranged tours for attendees/guests.

Please make your reservation by noting choice of tour. Pre-sold tickets will be held at the tour desk located in Hall 4C of the Washington State Convention and Trade Center. Please arrive 15 minutes prior to departure time.

Registration:

To register for the tours, please complete and return the registration form along with full payment to:

Convention Services Northwest, Attn: Becky Haiduck
Tower Building/Suite 1414,1809 Seventh Avenue, Seattle, WA 98101, USA
PHONE: (206) 292-9198 • FAX: (206) 292-0559

*** PLEASE CHOOSE ONLY ONE OPTION FOR SENDING FORM ***

Description	Date/Time	Price	No.	Amount
Sample Seattle – A Deluxe City Tour	Monday, February 18, 2002 – 9:00am-12:30pm	$28	________	$________
Historic Port Townsend Day Trip	Tuesday, February 19, 2002 – 9:00am-4:30pm	$59	________	$________
Wine Tasting Tour	Wednesday, February 20, 2002 – 1:00pm-5:00pm	$39	________	$________
			Total	$________

Last Name ______________________ First Name ______________________ MI __________

Street Address ____

City ______________________ State/Country ______________________ Zip/Postal Code __________

Daytime Phone ______________________ Fax ______________________

E-mail ____

☐ I have special needs, disabilities or dietary concerns. Please have someone from Convention Services Northwest contact me.

Payment options:

☐ Check or Money Order Enclosed (remit in US funds)

☐ American Express ☐ MasterCard ☐ VISA ☐ Discover ☐ Diners

Account Number ______________________ Expiration Date ______________________

Card Holder Name ______________________ Authorized Signature ______________________

Reservations:

Reservations must be received by January 16, 2002. Tickets may be purchased on-site on a space-available basis only and tickets will include an additional $2.00 charge. You may pick up your tickets at the Washington State Convention and Trade Center in Hall 4C staring at 11:00am on Sunday, February 17, 2002.

Refunds:

Refunds for cancellations will be made if written request is received at the Convention Services Northwest office by January 16, 2002, less a $5.00 handling fee per ticket. After January 16, 2002, no refunds or exchanges can be made. If minimum registration on a tour is not met, Convention Services Northwest will refund the cancelled tour or apply the refund towards another tour.

For Office Use Only:

Deposit No. ______________________ Amount $ ______________________

Check No. ______________________ Inn. ______________________

CONFERENCE PROCEEDINGS

THE FOLLOWING TITLES WILL BE AVAILABLE AT THE MEETING. RESERVE YOUR COPY USING THE TMS ANNUAL MEETING REGISTRATION FORM.

CALPHAD and Alloy Thermodynamics

Patrice E.A. Turchi, Antonios Gonis, and Robert D. Shull, editors

These proceedings emphasize all theoretical aspects of computational thermodynamics and kinetics and their impact on the science of alloys and materials design. The book will provide an assessment of the CALPHAD (Calculation of Phase Diagrams) approach pioneered by 2002 Hume-Rothery Award recipient Larry Kaufman, a review of the current status of the software applications based on the CALPHAD approach, the impact of CALPHAD on alloy thermodynamics and design, and future prospects. The book will provide a detailed picture of the development of CALPHAD and point to further research.

ISBN 0-87339-514-X

Approx. 390 pp., illus., index, hardcover

Order No. 514X

Member price: $72

Computational Modeling of Materials, Minerals, and Metals Processing

M. Cross, J.W. Evans, and C. Bailey, editors

This set contains the proceedings, in both print and CD-ROM formats, of the Computational Modeling of Materials, Minerals, and Metals Processing Symposium to be held at the 2002 TMS Annual Meeting in Seattle, Washington.

Computational models offer an effective way to design, analyze, and optimize materials, metals, and minerals processing. Computational modeling is increasingly becoming the means by which every factor in the operation of a process can be analyzed in a rational manner. Such models also represent a framework for much of our understanding of process operations.

This international symposium brings together participants from all aspects of computational modeling of materials, minerals, and metals processing, including the engineers involved primarily in specific applications, developers of computational modeling tools, and the developers of models. This allows all involved to understand the most recent advances in this rapidly developing enabling technology.

ISBN 0-87339-513-1

Approx. 700 pp., illus., index, hardcover & CD-ROM

Order No. 5131

Price: $129

Creep Deformation: Fundamentals and Applications

Rajiv S. Mishra, James C. Earthman, and Sai V. Raj, editors

These proceedings focus on the application of fundamental creep research to the design and development of high temperature materials for engineering applications. The book deals with all aspects of creep deformation and high temperature materials development, specifically the influence of microstructures on various aspects of creep and the application of this information in the design of highly creep resistant materials. Emphasis will be placed on advanced ceramic and metal matrix composites and advanced intermetallics.

This volume brings together researchers working on fundamental issues relating to the development and characterization of high temperature materials and design engineers involved in high temperature applications.

ISBN 0-87339-515-8

Approx. 415 pp., illus., index, hardcover

Order No. 5158

Member price: $105

Light Metals 2002

Wolfgang Schneider, editor

Held at the TMS Annual Meeting & Exhibition each year, the Light Metals series has become the definitive annual reference source in the field of aluminum production and related light metals technologies. Each volume contains complete coverage of advancements and current work in cast shop technology, alumina and bauxite, carbon technology, aluminum reduction technology, and recycling. In addition, Light Metals 2002 includes coverage of reactive metals and advances in molten salt processing technology. Light Metals 2002 is sold as a package that includes the proceedings in both hardcover and text-searchable CD-ROM formats.

ISBN 0-87339-519-0

Approx. 1200 pp., illus., index, hardcover & CD-ROM

Order No. 5190

Member price: $158

EPD Congress 2002

Patrick R. Taylor, editor

The Extraction & Processing Division Congress, held at the TMS Annual Meeting & Exhibition each year, has become the definitive annual forum for new technological developments in the process metallurgy community. This volume will also include the proceedings of the Fundamentals of Advanced Materials for Energy Conversion symposium.

In addition to general abstracts, this year's edition will include papers on:

- Modeling of high temperature alloy processing
- General pyrometallurgy
- Generation, treatment, metal recovery, and disposal of flyash
- Imaging of dynamic processes
- Materials processing fundamentals
- General recycling of materials

ISBN 0-87339-516-6

Approx. 812 pp., index, hardcover

Order No. 5166

Member price: $96

High-Cycle Fatigue, the David L. Davidson Symposium

Kwai S. Chan and Peter K. Liaw, editors

These proceedings from the David L. Davidson Symposium on High-Cycle Fatigue review the current research activities and assess the state-of-the-art in high-cycle fatigue, which has become a major concern in the design of engineering components and structures. This volume will include papers on a basic understanding of failure mechanisms, experimental methods and studies, modeling and simulation, and life-prediction methodology. This volume will also contain papers from the Fatigue of High Temperature Alloys Symposium, which deals with fatigue behavior of high temperature alloys, including crack initiation and propagation modes.

ISBN 0-87339-518-2

Approx. 350 pp., index, hardcover

Order No. 5182

Member price: $110

High Performance Metallic Materials for Cost-Sensitive Applications

F.H. (Sam) Froes and Lu Li, editors

These proceedings will examine the most recent advances and best practices in structural materials selection, design, and manufacturing for producing affordable components, with a focus on titanium, aluminum, and other advanced metallic materials. This volume will discuss melting, casting, powder metallurgy, forging, forming, extrusion, and machining, as well as processing advances, innovative processing techniques, process modeling and materials by design, new alloys, and related processing-microstructure-properties-performance-cost studies.

ISBN 0-87339-522-0

Approx. 295 pp., index, PDF publication

Order No. 5220

Member price: $117

Sulfide Smelting 2002

Robert L. Stephens, and H.Y. Sohn, editors

These proceedings focus on all aspects of the pyrometallurgical production of primary metals from sulfide concentrates. Papers discuss industrial operations producing copper and nickel and the direct production of lead and zinc. Key topic areas include smelting and converting processes, recently completed capital projects, current operating practices, the predicted future of sulfide smelting operations, furnace integrity and refractory design, gas handling processes and equipment, issues related to the treatment of high-strength sulfur dioxide-containing off-gases, the production of alternative sulfur products, the treatment of acid plant blowdown streams and sulfated smelter dusts, and the capture and treatment of fugitive emissions.

ISBN 0-87339-525-5

Approx. 600 pp., illus., index, hardcover

Order No. 5255

Member price: $70

Advances in Metallic Glasses: Mechanical and Other Physical Properties, and Applications - I

Sponsored by: Electronic, Magnetic & Photonic Materials Division,
Program Organizers: K. F. Kelton, Washington University, Department of Physics, St. Louis, MO 63130 USA; A. L. Greer, University of Cambridge, Department of Materials Science & Metallurgy, Cambridge CB2 3QZ UK; Krishna Rajan, Rensselaer Polytechnic Institute, Department of Materials Science and Engineering, Troy, NY 12180-3590 USA

Wednesday AM February 20, 2002 | Room: 212 | Location: Washington State Conv. & Trade Center

Session Chairs: Joseph S. Poon, University of Virginia, Dept. of Phys., McCormick Rd., Charlottesville, VA 22904 USA; A. R. Yavari, Institut National Polytechnique de Grenoble, LTPCM-CNRS umr 5614, BP75, 38402 St.-Martin-d'Heres Campus, France

8:30 AM Invited
Civilian Research on Bulk Metallic Glasses Sponsored by the European Union: *A. R. Yavari*[1]; [1]Institut National Polytechnique de Grenoble, (LTPCM-CNRS umr 5614), BP 75, 38402 St-Martin-d'Hères Campus France

With near 2% elastic strain range (as compared to 0.2% for crystalline materials), BMGs have excellent values of the Ashby performance index σ^2/E (where σ and E are the yield strength and Young's modulus). High values of this performance index (reversible storing of elastic energy) open applications in sporting goods materials (golf clubs, skis, other high elasticity equipment), cutting, writing, punching and printing tools, springs, gears for micromachines (MEMS parts) and others. In this work we report on the results obtained by the European Union Network on BMGs. This Network brings together 9 research teams in 5 EU and 1 Associated states and the European Synchrotron (ESRF) facilities possessing the fundamental and engineering knowledge-base and equipment required to establish a European pole of excellence for research on BMG.

9:00 AM
Welding Technologies of Bulk Metallic Glasses: *Yoshihito Kawamura*[1]; Yasuhide Ohno[1]; [1]Kumamoto University, Matls. Sci., 2-39-1 Kuro-kami, Kumamoto 860-8555 Japan

The bulk metallic glasses have solved two main problems in metallic glasses, namely, the limitation of product size and the lack of workability. The problem of welding is, however, still unsolved. We have succeeded in welding bulk metallic glasses to bulk metallic glasses or crystalline materials with keeping the amorphous structure by friction, pulse-current and explosion methods. The tensile strength of the welded bulk metallic glasses was the same as that of the parent bulk metallic glasses. The friction welding is a solid state process where we used the superplasticity of the supercooled liquid. The pulse-current and explosion welding methods are liquid state processes where we used the high glass forming ability of the bulk metallic glasses and the high thermal stability of the supercooled liquid. The successful results obtained in this study are expected to push forward the application of bulk metallic glasses.

9:20 AM
Microstructure-Magnetic Properties Relationship in Bulk $Nd_{90-x}Fe_xAl_{10}$ Glassy Alloys: *Nicoleta Lupu*[1]; Horia Chiriac[1]; [1]National Institute of Research and Development for Technical Physics, Magnetic Matls. & Dev., 47 Mangeron Blvd., Iasi 6600 Romania

Rapidly and slowly quenched $Nd_{90-x}Fe_xAl_{10}$ glassy alloys with thicknesses up to 3 mm were investigated comparatively by structural (XRD, neutron scattering and calorimetric measurements) and magnetic AC and DC measurements in the temperature range 5-800K and external fields up to 10 T. These amorphous alloys crystallize through single exothermic peak and exhibit very large values for the reduced crystallization temperature, T_x/T_m, of 0.87 to 0.92. The glass-forming ability decreases with the Fe content increase. The mechanisms that govern the different magnetic behavior in rapidly quenched and respectively slowly quenched $Nd_{90-x}Fe_xAl_{10}$ glassy alloys are related to the cooling rates values assured in those two methods of preparation and will be discussed in detail. The large values of the coercive field obtained for $Nd_{90-x}Fe_xAl_{10}$ glassy alloys are ascribed to the existence of one non-equilibrium or metastable magnetic phase consisting in very small clusters whose sizes approach few nanometers.

9:40 AM
Synchrotron X-Ray Measurements of Lattice Strains during In-Situ Loading of Partially-Crystallized Bulk-Metallic-Glass Composites: Dorian K. Balch[1]; Ersan Üstündag[2]; *David C. Dunand*[1]; [1]Northwestern University, Dept. of Matls. Sci. & Eng., MLSB 2036, 2225 N. Campus Dr., Evanston, IL 60208-3108 USA; [2]California Institute of Technology, Dept. of Matls., Pasadena, CA 91125 USA

High-intensity synchrotron x-rays were used to study the micromechanics of load transfer upon uniaxial compressive loading of a Bulk-Metallic-Glass (BMG) composite containing 5 vol.% Ta particles. Diffraction rings were recorded for both the Ta particles and crystalline inclusions within the BMG matrix, which were produced by partial crystallization of the BMG and acted as crystalline "markers" in the amorphous matrix. Using elastic constants of each phase, the stresses are then calculated in the matrix and reinforcement of the composite. Load transfer between BMG and Ta is discussed in terms of plastic deformation of the Ta phase, integrity of the BMG/Ta interface and creep relaxation of the BMG matrix after a hold of 1 hour at the maximum uniaxial stress of 1250 MPa.

10:00 AM Break

10:20 AM
Mechanical Response of Zr-Based Metallic Glass: *Alla V. Sergueeva*[1]; Nathan Mara[1]; Amiya K. Mukherjee[1]; [1]University of California, Cheml. Eng. & Matl. Sci., 1220 Bainer Hall, Davis, CA 95616 USA

The new family of Zr-based multicomponent metallic glasses shows a beneficial combination of yield strength value as high as 2 GPa and microplasticity of up to 1% at room temperature and an excellent glass-forming ability in a wide supercooled liquid region. Partial devitrification of glassy alloys upon heating or hot working above the glass transition temperature can lead to formation of nanocrystalline precipitates in the glassy matrix. In this case, the mechanical properties depend on the amount of crystalline precipitates. The nature of the brittle crystalline intermetallic phases is likely to dominate the mechanical behavior with crystallization more than 50%, leading to the observed decrease in ductility for the annealed samples since the deformation is no longer governed by the deformation mechanism of the amorphous phase. A fully crystallized alloy produced by annealing revealed increasing ductility with temperature in the regime where grain growth occurs and this microstructure exhibited the superplastic deformation with high elongation at 650-700°C.

10:40 AM
Superplasticity in a Bulk Amorphous Pd-40Ni-20P Alloy: *Jinn P. Chu*[1]; C. L. Chiang[1]; T. G. Nieh[2]; Y. Kawamura[3]; [1]National Taiwan Ocean University, Inst. of Matls. Eng., No. 2, Pei-Ning Rd., Keelung 20224 Taiwan; [2]Lawrence Livermore National Laboratory, L-350, PO Box 808, Livermore, CA 94551 USA; [3]Kumamoto University, Dept. of Mechl. Eng. & Matls. Sci., Kumamoto 860-8555 Japan

Recent advances in metallic glasses that have high glass-forming ability and high thermal stability have launched a number of studies on fundamental science and practical applications. In the present study, compressive deformation behavior of a bulk amorphous Pd-40Ni-20P alloy was characterized in the supercooled liquid region. Significant reductions in sample height (>95%) were achieved after deformation, suggesting the possible superplastic-like behavior in the alloy. Structures of the amorphous material, both before and after deformation, were examined using X-ray diffraction and differential scanning calorimetry. Transmission electron microscopy was also used to examine the deformed samples. The superplastic-like behavior will be presented and discussed in light of the microstructure/crystal structure results.

11:00 AM
Effect of Plasticity on the Elastic Modulus and Density of Bulk Amorphous $Pd_{40}Cu_{30}Ni_{10}P_{20}$: *Ulrich Harms*[1]; Ou Jin[1]; Ricardo B. Schwarz[1]; [1]Los Alamos National Laboratory, Struct./Prop. Relations Grp., MS G755, Los Alamos, NM 87545 USA

Although free volume is often used to characterize structural changes in amorphous metals, few density measurements have been reported. We measured the effect of annealing and plastic deformation on the density and modulus of bulk amorphous $Pd_{40}Cu_{30}Ni_{10}P_{20}$. The shear and bulk modulus are measured by a resonant-ultrasound method. The density is measured with a resolution of 1 part in 10,000. Whereas annealing causes the shear modulus and density to increase, the bulk modulus remains approximately constant. Plastic deformation reduces both the density and shear modulus to their values in the as-quenched state. We find a linear relationship between the shear modulus and density changes, suggesting that these parameters could be described by a single type of defect. The relative change in the shear modulus is approximately 30 times larger than the relative change in the density. Models for the ratio of density to modulus change are discussed.

11:20 AM
Mechanical Behavior of In-Situ Formed Bulk Metallic Glass Matrix Composites: *Bjorn Clausen*[1]; Seung-Yub Lee[1]; Ersan Üstündag[1]; C. P. Kim[1]; Mark A.M. Bourke[2]; Donald W. Brown[2]; [1]California Institute of Technology, Matls. Sci., 1200 E. California Blvd., MC 138-78, Pasadena, CA 91125 USA; [2]Los Alamos National Laboratory, MST-8, PO Box 1663, MS H805, Los Alamos, NM 87545 USA

Bulk metallic glass (BMG)-matrix composites have recently been developed to increase the ductility of BMGs. One of the most promising composites is the in-situ-formed BMG/"β-phase" composite. Here, the "β-phase" is a fine dendritic structure of a BCC crystalline alloy and precipitates during casting. This phase has been shown to inhibit the formation of macroscopic shear bands that cause catastrophic failure in monolithic BMGs under unconstrained loading. In this study, we have used neutron diffraction to measure the elastic deformation in the crystalline "β-phase" during mechanical loading of BMG/"β-phase" composites and compared this to the deformation of "β-phase" monoliths. We have employed self-consistent deformation models to interpret the diffraction data and to deduce additional parameters such as single-crystal elastic constants. The results suggest that the mechanical properties of the "β-phase" are highly variable and sensitive to processing conditions.

11:40 AM
Acoustic Emission Investigation of Inhomogeneous Plastic Flow of Metallic Glasses: *Vitaly Khonik*[1]; Alexey Vinogradov[2]; [1]State Pedagogical University, Dept. of Gen. Phys., Lenin St. 86, Voronezh 394043 Russia; [2]Osaka City University, Dept. of Intelligent Matls. Eng., Sugimoto 3-3-138, Sumiyoshi-ku, Osaka 558-8585 Japan

A complex statistical and spectral analysis of acoustic emission (AE) during plastic flow of metallic glasses is performed aiming at clarification of mechanisms of their inhomogeneous plastic deformation. The AE power spectra and waveforms of individual signals are analyzed in detail. The onset and kinetics of shear band nucleation have been clearly detected by means of AE. Possible mechanisms of inhomogeneous deformation are discussed in light of AE results.

Alumina and Bauxite: Alumina Industry Trends, Products, Environment

Sponsored by: Light Metals Division, Aluminum Committee
Program Organizers: Jacques M. Mordini, Aluminium Pechiney, Gardanne, Cedex 13541 France; Steve Rosenberg, Worsley Alumina Pty, Ltd., Process Chemistry Group, Collie, West Australia 6225 Australia; Wolfgang Schneider, VAW Aluminium AG, Research & Development Manager Cast Technology, Bonn 53177 Germany

Wednesday AM February 20, 2002 — Room: 609 — Location: Washington State Conv. & Trade Center

Session Chair: TBA

8:30 AM Invited
The Alumina Industry Technology Roadmap: *Ivan Anich*[1]; [1]Alcoa World Alumina, PO Box 252, Applecross, Western Australia 6153 Australia

In an unprecedented global collaboration, more than 30 international leaders in the alumina refining industry have reached a consensus on the R&D activities needed to address the technical challenges over the next 20 years. The result is the Alumina Industry Technology Roadmap, a strategic plan containing a goal-based R&D agenda that can be pursued by both individual companies and collaborative partnerships between companies, government and other members of the research community. The framework was a set of explicit targets for reducing capital and operating costs; improving energy efficiency; enhancing environmental performance, safety and health; and meeting customers' needs. An alumina techniology committee has been established as a focal point for implementation of the roadmap. The roadmap was coordinated by AMIRA International, and supported by the US Department of Energy; the Australian Department of Industry, Science and Resources; the Aluminium Association; the Australian Aluminium Council; and the Government of Western Australia.

9:00 AM
Extraction of Aluminium Oxide from Bauxite and Redmud: *Vilas D. Tathavadkar*[1]; M. P. Antony[2]; Animesh Jha[1]; [1]University of Leeds, Dept. of Matls., Clarendon Rd., Leeds, W. Yorkshire LS2 9JT UK; [2]Post-Irradiation Studies Section, Fuel Chem. Div., IGCAR, Kalpakkam, TN 603 102 India

Pure alumina (Al2O3) is generally extracted from bauxite via the Bayer process. A complete recovery of alumina is economically not possible via this process. The safe disposal of process residue, red mud, is one of the disadvantages of Bayer process. A novel route for extracting alumina from bauxite has been developed. The process involves roasting of bauxite with an alkali carbonate in air at temperatures above 1050K. The roasted mass is digested in water and filtered. Al(OH)3 is precipitated by adjusting the pH of the solution. Pure alumina is produced by calcining the Al(OH)3 precipitate. The extraction efficiency of alumina is more than 98%. Alkali carbonates can be recovered by evaporating the filtrate after removing Al(OH)3 precipitate. A mechanism based on XRD and SEM of the roasted product is proposed. Alumina from red mud can also be extracted in a similar way. Based on the alkali-roasting technique a zero-waste technology for alumina extraction can be devised.

9:25 AM
Effect of Thermal Pretreatment on Grindability and Upgradation of Bauxite for Refractory Applications: R. Bhima Rao[1]; *M. B. Veeresh*[1]; G. N. Banerjee[1]; [1]Karnataka University, Dept. of Minl. Procg., Regional Rsrch. Lab., (Council of Scientific & Indl. Rsrch.), Bhubaneswar-751013 India

Iron is a detrimental element in bauxite used for refractory applications. A process has been developed in the laboratory on removal of iron and improvement in alumina recovery of bauxite by reduction/calcination roasting followed by magnetic separation. For effective liberation of mineral the ore is to be comminuted to the desired fineness. As this process is energy intensive, a study has been undertaken on determination of overall energy requirement for grinding of ore as well as ore samples were subjected to various pretreatments as reduction roasting with coke/calcination-quenching in water at room temperature for effective liberation of minerals. It has been found that the thermal pretreatment method has several advantages in terms of grinding time, magnetic intensity, alumina recovery, compared to the crude ore.

9:50 AM Break

10:10 AM Cancelled
Boiler Efficiency Improvements in a Bayer Process Plant: *Walters Leighton*

10:35 AM
Future of Guinea Bauxite Mining and Alumina Industry Development: *Siafa Coulibaly*[1]; [1]Ministry of Mines, Geology and Environment, Conakry Guinea

This paper discusses the various aspects of the future alumina-bauxite industry in Guinea. Guinea is endowed with enormous reserves of bauxite estimated to several billion tons of good grade material within 200 kms of the coast, plus a major bauxite province along the northeast slope of the Fouta Djallon mountain. Guinea bauxite reserves development has, over the past forty years, been focused on three specific areas not far from the coast: Fria deposits, Compagnie des Bauxites de Guinée, Compagnie des Bauxites de Kindia formerly SBK. Guinea geographic location, particularly in regard to European, North American and African markets is quite favourable. It is also a fact that Guinea has a relatively untapped hydroelectric potential based on the Konkouré river which flows into the Atlantic ocean. The larger project, located 40 kms upstream from Fria is Kaleta-Souapiti, estimated at 1000 MW. Guinea coastal and internal infrastructure is reasonable, but needs improvement.

Aluminum Reduction Technology: Cathode Materials –Joint Carbon Technology

Sponsored by: Light Metals Division, Aluminum Committee
Program Organizers: Martin Segatz, VAW Aluminum AG, D-53117, Bonn Germany; Halvor Kvande, Norsk Hydro ASA, Oslo N-0240 Norway; Wolfgang Schneider, VAW Aluminium AG, Research & Development Manager Cast Technology, Bonn 53177 Germany

Wednesday AM	Room: 6B
February 20, 2002	Location: Washington State Conv. & Trade Center

Session Chair: Siegfried Wilkening, VAW Aluminium-Technologie GmbH, Georg-v-Boeselagerstr. 25, Bonn 53117 Germany

8:30 AM
Anthracite Evaluation for Amorphous Cathodes: *Frank Hiltmann*[1]; Boguslawa Jesionek[2]; Janusz Tomala[2]; Maciej Bojkowski[3]; [1]SGL Carbon GmbH, Griesheim Plant, Stroofstrasse 27, Frankfurt 65933 Germany; [2]ZEW S.A., ul Piastowska 29, Raciborz 47-400 Poland; [3]SGL Carbon S.A., ul. Wegierska, Nowy Sacz 33-300 Poland

One of the key factors for production of high quality cathodes is the selection of proper raw materials. Especially for amorphous cathodes, which usually contain 50-70% of gas or electrically calcined anthracite, the right choice is essential with regard to the higher chemical sensitivity of anthracite vs. graphite. The process of characterizing green anthracites, with emphasis on petrographic analyses, is described and a classification system presented. The lab procedure for estimating the calcination behavior is outlined and the suitability for use in cathode manufacture discussed.

8:55 AM
Porosity Modifications in the Carbon Cathode of Aluminum Reduction Cell II: *Mohamed Othman Ibrahiem*[1]; S. M. El-Raghy[2]; F. M. Ahmed[1]; [1]Aluminum Company of Egypt, R&D Dept., Nag-Hammadi Egypt; [2]Cairo University, R&D Dept., Nag-Hammadi Egypt

In a previous study, reduction of cathode porosity was achieved by impregnation with a high carbon yield resin (furfuryl alcohol), followed by curing and pyrolysis for several cycles. The aim of this study was further characterization and investigation under electrolysis conditions. Thermal conductivity increased from 7.66 W/mK to 10.45 W/mK when the open porosity decreased from 15% to 1% by multiple impregnation/pyrolysis cycles. An increase in ash content was observed as a function of impregnation cycles. The influence of applied current has been studied with a current density of 0.7 A/cm2 in a basic cryolite-alumina melt for durations up to 3 hours. The investigation included measurement of sodium entry, ash content, thermal conductivity, compressive strength, specific electrical resistance, and structure by optical microscopy. Passing electric current increases the sodium level in the cathode and increases its electrical and thermal conductivity. Modified cathodes are less reactive under working conditions.

9:20 AM
A New Ramming Paste for the Aluminum Electrolysis Cell Fitting with Technical and Environmental Issues: Daniel Dumas[1]; Simon Meseguer[1]; Regis Paulus[1]; *Serge Lacroix*[2]; [1]Carbone Savoie, R&D Dept., 30, Rue Louis Jouvet, BP 16, Venissieux, Cedex 69631 France; [2]UCAR SNC, Apply Tech., La Léchère, Aigueblanche 73264 France

The ramming paste is known to be a key material in the Aluminum electrolysis cell. The paste must have the relevant properties to avoid poor pot performances. In addition the emission of hazardous compounds must be at the lowest possible level during densification and baking. Coal tar pitch usually used as binder for the ramming pastes contains polycyclic aromatic hydrocarbons, some of which are classified as genotoxic. The present work describes how to decrease significantly the polycyclic aromatic hydrocarbon emissions by using the appropriate binder while maintaining the relevant characteristics of the cold ramming paste regarding pot performances. The data obtained in test pots are included.

9:45 AM
Use of Ceramic Materials for Filling Joints in Cell Cathode Blocks: *Gennadiy Vladimirovich Solonin*[1]; Michail Alexandrovich Fridman[1]; Vladimir Kuzmich Nikitenko[1]; [1]JSC "Zaporozhye Aluminum Works" (ZALK), 15, Yuzhnoye Shosse, Zaporozhye 69032 Ukraine

The need to improve performance characteristics of cathode lining, in particular to increase cell life, is driven by the high cell repair costs and the disposal of environmentally harmful wastes formed during the reduction cell relining. This paper presents a method of improving the performance characteristics of the cathode blocks in an aluminium reduction cell. A procedure has been developed and the results of the laboratory tests of ceramic materials used in the cathode joints are given. It has been shown that the resistance of joint materials to the melt attack is determined by the porosity of the materials used. The experimental and industrial test results of using a slip casting procedure for filling the cathode blocks joints are given. The results achieved made it possible to eliminate the use of carbon ramming paste from the cathode relining procedure. It has been demonstrated that after the introduction of the new cell relining procedure, there were no premature cell failures even under long electric power outages. Other positive effects of the procedure presented have also been achieved.

10:10 AM Break

10:20 AM
The Role of Silica Rich-Low Permeability Bricks in Multilayer Barrier Design of Aluminum Electrolytic Cells: Don Harris[1]; John Lam[1]; *George Oprea*[2]; [1]Clayburn Refractories, Ltd., 33765 Pine St., Abbotsford, BC V2S 5C1 Canada; [2]University of British Columbia, Dept. of Metals & Matls. Eng., 309-6350 Stores Rd., Vancouver, BC V6T 1Z4 Canada

Multilayer barrier designs that employ a combination of different refractories, are standard practices for numerous aluminum smelters. While operating results confirmed the efficiency of such systems, no laboratory work or testing methods had been presented to confirm the effectiveness nor the optimization of the combination of bricks utilized. This paper discusses a test method comparing different refractory brick compositions when exposed to various cryolitic-based environments, simulating the changes in bath chemistry beneath the cathode. The penetration and corrosion results were correlated with the testing parameters, the refractories' chemistry and microstructure as well as with the changes in reacted bath chemistry during penetration.

10:45 AM
Aging of Cathode Refractory Materials in Aluminium Reduction Cells: *Rikke Weibel*[1]; Leo Fisher Juhl[1]; Bent Nielsen[1]; Joergen Mikkelsen[1]; Ole-Jacob Siljan[2]; Kjeld Thovsen[2]; Sara Thornblad Mathisen[2]; [1]Skamol, Oestergade 58-60, Nykoebing DK-7900 Denmark; [2]Hydro Aluminium, Rsrch. Ctr. Porsgrunn, PO Box 2560, Porsgrunn N-3901 Norway

Aging of refractory materials during cell life has been studied in respect to changes in thermal conductivity and consequently influence on the heat balances. Autopsies have been performed on electrolytic cells with ages ranging from 500 days to 3200 days. Samples from different positions and layers in the cells, and of three different insulating materials are represented. Thermal conductivity measurements of the small autopsy samples have been performed by the Hot Disk method. During operation of the reduction cells the thermal conductivity of the pot lining material may change substantially (according to position in the cell, which is related to the degree of compression, precipitation of solids in pores, etc.) The physical properties of the virgin material (density, porosity, compressibility, etc.) also influences on the changes in thermal conductivity. The measured general increase in thermal conductivity of "spent" pot lining materials compared with similar virgin materials reflects the necessity of increasing cell voltage gradually during cell life in order to compensate for increased heat loss. Modelling of heat balances have been based on the thermal conductivity measurements on autopsy samples from three different ways of insulating the cathode construction, comparing two grades of moler bricks (HIPOR and SUPRA) with a combination of calcium silicate (SUPER-1100 E) and moler bricks (SUPRA). Heat balance modelling has showed that the lowest possible thermal conductivity of the insulating material is not the only important factor, also the evolution of the thermal conductivity over time is important (SUPER-1100 E versus HIPOR versus SUPRA).

11:10 AM
Environmental and Economic Aspects of an Effective Diffusion Barrier: *E. Sturm*[1]; J. Prepeneit[1]; [1]Hamburger Aluminium-Werk GmbH, Hamburg 21129 Germany

In pot lining there is a long history of more or less effective diffusion barriers. Some aspects of SPL, the need of reusing materials and further lowering of energy consumption has to be regarded. At HAW a double layer barrier in combination with alumina insulation has been experimented over more than 2000 days. The influence on heat balance has to be taken into account within a total lining concept, that includes cathode type and pot shell changes. The energy saving derives from a decrease in pot voltage of 50 mV. The mass balance of bath additives, impurities and fluorid is changed. Due to bath production there is a demand for low content of Na20 in alumina. Waste dumping of lining materials using alumina as insulation can be reduced. The cost balance of all the previous aspects reveals an economic solution.

11:35 AM
Aluminum-Steel Electrical Transition Joints, Effects of Temperature and Time upon Performance: *John G. Banker*[1]; Antoine Nobili[2]; [1]Dynamic Materials Corporation, Clad Metal Div., 5405 Spine Rd., Boulder, CO 80301 USA; [2]Dynamic Materials Corporation, Nobelclad Div., 1 Allee Alfred Nobel, Rivesaltes, 66600 France

Aluminum-steel electric transition joints (ETJ) are often used in aluminum and magnesium reduction cells for making welds between aluminum buss and steel anodes and cathodes. Depending upon the cell design and operation, ETJ's can operate at temperatures ranging between 200°C and 500°C, possibly hotter. Over time, these thermal conditions can have significant deleterious effect upon the ETJ bond strength, resulting in eventual failure. A detailed study was performed measuring ETJ bond strength as a function of time, temperature, and design. Specimens were maintained at temperatures of 300°C to 600°C for up to one year, and then tensile tests were performed. Metallographic and spectrographic analyses were performed to analyze the mechanism of bond degradation. Diffusion and subsequent intermetallic formation were the mechanisms causing bond degradation. Theoretical diffusion equations provide a basis for extrapolation of test data to longer time periods. The addition of a thin interlayer between the aluminum and steel can alter this behavior. Several interlayer materials were evaluated, including chromium and titanium. Titanium provided the most significant improvement in performance. Extrapolations indicate that titanium interlayer ETJ's can be expected to operate for over 10 years at 450°C without significant degradation.

Aluminum Sheet and Plate Rolling & Finishing Technology and Applications: Aluminum Sheet and Plate Processing

Sponsored by: Light Metals Division, Aluminum Association, *Program Organizers:* Michael H. Skillingberg, The Aluminum Association, Inc., Washington, DC 20006 USA; John P. Brandimarte, Precision Coil, Inc., Clarksburg, WV 26302-2650 USA; Karl Eminger, Alcoa, Inc., Alcoa Mill Products, Lancaster, PA 17604 USA; Seymour G. Epstein, The Aluminum Association, Inc., Washington, DC 20006 USA; Jeff J. Kadilak, Alcan, Inc., Oswego, NY 13126 USA; Leland R. Lorentzen, Nichols Aluminum, Davenport, IA 52801 USA; Douglas N. McLeod, ARCO Aluminum, Inc., Louisville, KY 40242 USA; Ken Schreckengast, Coastal Aluminum Rolling Mills, Inc., Williamsport, PA 17701 USA

Wednesday AM — Room: 608
February 20, 2002 — Location: Washington State Conv. & Trade Center

Session Chair: Jeff J. Kadilak, Alcan, Inc., PO Box 28, Oswego, NY 13126 USA

8:30 AM
Strip Casting Technology-A Key to Product Quality: *Frederic Basson*[1]; Pierre-Yves Menet[1]; Klaus Maiwald[1]; Marc Bosch[1]; [1]Pechiney Aluminium Engineering, Continuous Casting Tech., Centr'alp, BP 24, Voreppe, Cedex 38341 France

Pechiney has been dedicated to developing twin roll casting of aluminum technology and products for more than 40 years. Lately a new generation of machines, the Jumbo 3CM, has emerged to complete the range of equipment available to produce hot rerolls on an economical basis. The Jumbo 3CM includes the latest technological developments that Pechiney has designed in order to: Reduce Casting gauge; Increase productivity and casting width; Increase quality of existing products and improve consistency of the cast quality; Develop new products from continuous cast sheet. The presentation reviews the numerous technological developments that are now commercially available: liquid metal treatment (Alpur, Pechiney Deep Bed Filter), patented metal feeding into the caster with accurate metal level control and temperature control, patented roll cooling system, improved coating control device (new release-agent spraying technology), cross and longitudinal profile monitoring, casting supervision system. These developments have made possible the casting of alloys for more demanding products such as can stock, thin gauge foil, litho sheet and automotive sheet. Existing casters can also benefit from these developments.

8:55 AM
Aluminium Strip & Foil Rolling-Leading Technologies on the Market: *Axel E. Barten*[1]; [1]Achenbach Buschhütten GmbH, Siegener Str. 152, Kreuztal D-57223 Germany

The production of wider and thinner aluminum light gauge strip and foil with best quality and high rolling speeds as well as short change times for a high productivity is the key to the success of a growing number of producers world wide. Advanced machinery, systems, controls and technology provided by Achenbach Buschhütten are necessary to reach this excessive goal. The OPTIROLL INTRAPLANT® adaptive automation system fulfills all requirements of modern rolling mill technology. Its big advantage lies in its modular design to be installed either in single components or as a complete system using all synergy effects of their combination. All movements and interlocks are realized in two levels in the OPTIROLL INTRAPLANT® System: The manual and the automatic control level. The new OPTIROLL® flatness measuring roll has been modified completely to optimize the measuring results. The fully digital flatness control system consists of four independent control loops. Roll tilting, work roll bending and variable crown are servo controlled. WIN Spray S® is the ultimate cooling system for aluminum rolling mills. The patented OPTIROLL -SGC® (Spacer Gauge Control) system with control parameters: roll separating force, adjustment cylinder position, mass flow, strip tensions and rolling speed is described.

9:20 AM
An Approach to Understanding Mill Vibration: *Thomas W.D. Farley*[1]; [1]Alcan International, Ltd., Southam Rd., Banbury, Oxon OX16 2SP UK

Alcan Inc. is a multinational company engaged in all aspects of the aluminium industry. This paper presents an approach adopted by Alcan to understand and solve mill vibration issues experienced on Alcan's cold rolling mills. The different types of mill vibration phenomena are described with reference to our current understanding. Predictions from a computer model of a mill stand are presented and compared to experimental measurements for 3rd and 5th Octave Chatter. Examples from other computer simulations are described that have been used to justify engineering projects to solve vibration problems.

9:45 AM
Roll Cooling Concepts: *Bernard J. Forster*[1]; *David Tucker*[2]; [1]Lechler, Inc., 445 Kautz Rd., Saint Charles, IL 60174 USA; [2]Lechler, Ltd., 1 Fell St., Newhall, Sheffield S9 2TP Great Britain

Properly cooling the rolls in a rolling mill is critical to product quality, product quantity and roll life. To accomplish it effectively, a thorough understanding of current coolant application theories and commonly used practices is necessary. Managing heat in a rolling mill begins with understanding how it is generated. Sources of heat include radiation, deformation, and friction. The role of coolant is to remove heat from the rolls, the product or both. How this is accomplished can affect performance factors such as product shape, roll life, and surface defects. Properly managing heat requires a consideration of several design parameters. The target surfaces, header location, and nozzle characteristics are among the many factors, which must be defined correctly. The purpose of this paper will be to define the current theories on roll cooling applications, compare them with popular application principles and establish a design methodology for effective and economical roll cooling.

10:10 AM Break

10:20 AM Cancelled
Coolant Mist and VOC Control Systems Applied to Hot and Cold Rolling Mills in the Aluminum and Steel Industry: *Richard W. Perryman*

10:45 AM
OPTIPURE-Integrative Filtration Technology for Economical and Ecological Efficiency: *Axel E. Barten*[1]; [1]Achenbach Buschhütten GmbH, Siegener Str. 152, Kreuztal D-57223 Germany

For aluminum rolling plants Achenbach Buschhütten is providing a complete rolling oil management package under the trade name of OPTIPURE® Filtration Technology, following an integrative system philosophy instead of offering "additions". By this way economical needs are ideally matched with ecological requirements of the rolling process. It gets feasible by the consequent pursuit of the "closed loop principle" in our OPTIPURE® technology as well as by the extremely high process efficiency of each and every component. Optimum results in rolling as well as highest regeneration rates of the processed rolling oils are achieved. At the same time negative influences on the environment on air, soil and water are minimized. All OPTIPURE®

systems are equipped with comprehensive visualization packages for online monitoring the automatic filtration process. Essentially, three different types of filtration systems are available: Fume Exhaust Filtration Systems for Rolling Mills: The AIRPURE® systems achieve a continuous recovery of evaporated roll coolants from the exhaust air combined with a complete oil treatment process in order to provide "new quality" rolling oil directly back to the rolling process. Micro-Filtration Systems for Roll Coolants: The SUPERSTACK®II horizontal plate filter systems are the ideal supplement by mechanically filtering all rolling generated particles full-stream out of the mill coolant. Modern filters have a CONDUSENS® sensor for on-line measurement of the electrical conductivity of poor conducting liquids. By measuring conductivity, dielectric permittivity and temperature of the rolling oil used in foil rolling, its contamination, the danger of uncontrolled discharges and the inherent fire risk are continuously determined. Rectification Systems for Roll Coolants: The WOR® systems "superpolish" roll coolants by removing non-mechanical contaminants such as tramp oils, thus closing the complete "recycling loop". These systems can be utilized as stand-alone devices. The strictly modular design allows to optimize each application for any specific mill requirement and to comply with the individual customers' requests. Therefore OPTIPURE® systems are not only the ultimate solution for new mills but also for the retrofit of existing ones. Applied in combination as an integrated system the user profits from all synergy effects between the single devices. These effects are: Minimized roll coolant consumption in the rolling process; Consistent high roll coolant quality; Minimized pollution of the environment by reduction of wastes; Optimum energy efficiency.

11:10 AM

Truly Universal Non-Contact Thickness Sensors: *Christopher Burnett*[1]; Gavin Carmichael[1]; Dino Jardina[1]; [1]Thermo-Radiometrie, Sensor & Electl. Dvlp., 9298 Gaither Rd., Gaithersburg, MD 20877 USA

The tight spaces, temperature variations and general environment of the numerous breeds and generations of rolling mills provide inherent physical limits for thickness sensor designs. Compounding these mechanical constraints, thickness sensors must provide higher performance to measure the seemingly infinite variations in alloy chemistries to tighter and tighter tolerances. Striking a balance of high performance and mechanical integrity has been an ongoing effort by gauge manufacturers. As the end market continues to engineer methods of producing more with less material, the gauge manufacturers must design sensors that provide higher performance in a smaller package. To answer the challenge presented by these limits, Thermo Radiometrie has developed a sensor to provide the performance of an x-ray based thickness sensor, capable of measuring from the thinnest foils up to the thicker sheet direct from the hot mill, all in the mill envelope equivalent to an isotope sensor.

11:35 AM

New Annealing Concept for Aluminum Coils: *Dominik Schroeder*[1]; Holger Kehler[1]; [1]Schmitz+Apelt LOI, Clausewitzstrasse 82, D-42389 Wuppertal, Germany

The options of rationalization of roller hearth or continuous strip annealing furnaces for aluminum coils are limited. A line of individual-chamber furnaces, raised above the floor and charged from underneath, renders new possibilities to increase the flexibility and economical operation of the annealing process. Each individual chamber anneals one (1) coil and is equipped with an indirect, natural gas-fired heating system, a high volume flow, variable speed circulation fan, and a cooling unit. Each furnace chamber uses its own PLC, allowing the chambers to operate independently of each other. The furnaces are designed for inert gas operation. The entire annealing process runs without oxygen. In order to save floor space, the chambers are charged from underneath by a mobile, scissors-type lifting table. This new annealing concept complies with all economic and quality requirements, such as: short heating and cooling times, exact temperature control, to prevent superheating at the coil's edges, high temperature accuracy during soak, individual annealing programs, energy-saving operation and minimum maintenance required. A plant's annealing capacity can be increased most easily by adding one or more additional chambers to the line.

Carbon Technology: Cathode Materials –Joint Aluminum Reduction Technology

Sponsored by: Light Metals Division, Aluminum Committee
Program Organizers: Martin Segatz, VAW Aluminum AG, D-53117, Bonn Germany; Halvor Kvande, Norsk Hydro ASA, Oslo N-0240 Norway; Wolfgang Schneider, VAW Aluminium AG, Research & Development Manager Cast Technology, Bonn 53177 Germany

Wednesday AM — Room: 6B
February 20, 2002 — Location: Washington State Conv. & Trade Center

Session Chair: Siegfried Wilkening, VAW Aluminium-Technologie GmbH, Georg-v-Boeselagerstr. 25, Bonn 53117 Germany

8:30 AM

Anthracite Evaluation for Amorphous Cathodes: *Frank Hiltmann*[1]; Boguslawa Jesionek[2]; Janusz Tomala[2]; Maciej Bojkowski[3]; [1]SGL Carbon GmbH, Griesheim Plant, Stroofstrasse 27, Frankfurt 65933 Germany; [2]ZEW S.A., ul Piastowska 29, Raciborz 47-400 Poland; [3]SGL Carbon S.A., ul. Wegierska, Nowy Sacz 33-300 Poland

One of the key factors for production of high quality cathodes is the selection of proper raw materials. Especially for amorphous cathodes, which usually contain 50-70% of gas or electrically calcined anthracite, the right choice is essential with regard to the higher chemical sensitivity of anthracite vs. graphite. The process of characterizing green anthracites, with emphasis on petrographic analyses, is described and a classification system presented. The lab procedure for estimating the calcination behavior is outlined and the suitability for use in cathode manufacture discussed.

8:55 AM

Porosity Modifications in the Carbon Cathode of Aluminum Reduction Cell II: *Mohamed Othman Ibrahiem*[1]; S. M. El-Raghy[2]; F. M. Ahmed[1]; [1]Aluminum Company of Egypt, R&D Dept., Nag-Hammadi Egypt; [2]Cairo University, R&D Dept., Nag-Hammadi Egypt

In a previous study, reduction of cathode porosity was achieved by impregnation with a high carbon yield resin (furfuryl alcohol), followed by curing and pyrolysis for several cycles. The aim of this study was further characterization and investigation under electrolysis conditions. Thermal conductivity increased from 7.66 W/mK to 10.45 W/mK when the open porosity decreased from 15% to 1% by multiple impregnation/pyrolysis cycles. An increase in ash content was observed as a function of impregnation cycles. The influence of applied current has been studied with a current density of 0.7 A/cm2 in a basic cryolite-alumina melt for durations up to 3 hours. The investigation included measurement of sodium entry, ash content, thermal conductivity, compressive strength, specific electrical resistance, and structure by optical microscopy. Passing electric current increases the sodium level in the cathode and increases its electrical and thermal conductivity. Modified cathodes are less reactive under working conditions.

9:20 AM

A New Ramming Paste for the Aluminum Electrolysis Cell Fitting with Technical and Environmental Issues: Daniel Dumas[1]; Simon Meseguer[1]; Regis Paulus[1]; *Serge Lacroix*[2]; [1]Carbone Savoie, R&D Dept., 30, Rue Louis Jouvet, BP 16, Venissieux, Cedex 69631 France; [2]UCAR SNC, Apply Tech., La Léchère, Aigueblanche 73264 France

The ramming paste is known to be a key material in the Aluminum electrolysis cell. The paste must have the relevant properties to avoid poor pot performances. In addition the emission of hazardous compounds must be at the lowest possible level during densification and baking. Coal tar pitch usually used as binder for the ramming pastes contains polycyclic aromatic hydrocarbons, some of which are classified as genotoxic. The present work describes how to decrease significantly the polycyclic aromatic hydrocarbon emissions by using the appropriate binder while maintaining the relevant characteristics of the cold ramming paste regarding pot performances. The data obtained in test pots are included.

9:45 AM

Use of Ceramic Materials for Filling Joints in Cell Cathode Blocks: *Gennadiy Vladimirovich Solonin*[1]; Michail Alexandrovich Fridman[1]; Vladimir Kuzmich Nikitenko[1]; [1]JSC "Zaporozhye Aluminum Works" (ZALK), 15, Yuzhnoye Shosse, Zaporozhye 69032 Ukraine

The need to improve performance characteristics of cathode lining, in particular to increase cell life, is driven by the high cell repair costs and the disposal of environmentally harmful wastes formed during the reduction cell relining. This paper presents a method of improving the performance characteristics of the cathode blocks in an aluminium reduction cell. A procedure has been developed and the results of the laboratory tests of ceramic materials used in the cathode joints are given. It has been shown that the resistance of joint materials to the melt attack is determined by the porosity of the materials used. The experimental and industrial test results of using a slip casting procedure for filling the cathode blocks joints are given. The results achieved made it possible to eliminate the use of carbon ramming paste from the cathode relining procedure. It has been demonstrated that after the introduction of the new cell relining procedure, there were no premature cell failures even under long electric power outages. Other positive effects of the procedure presented have also been achieved.

10:10 AM Break

10:20 AM
The Role of Silica Rich-Low Permeability Bricks in Multilayer Barrier Design of Aluminum Electrolytic Cells: Don Harris[1]; John Lam[1]; *George Oprea*[2]; [1]Clayburn Refractories, Ltd., 33765 Pine St., Abbotsford, BC V2S 5C1 Canada; [2]University of British Columbia, Dept. of Metals & Matls. Eng., 309-6350 Stores Rd., Vancouver, BC V6T 1Z4 Canada

Multilayer barrier designs that employ a combination of different refractories, are standard practices for numerous aluminum smelters. While operating results confirmed the efficiency of such systems, no laboratory work or testing methods had been presented to confirm the effectiveness nor the optimization of the combination of bricks utilized. This paper discusses a test method comparing different refractory brick compositions when exposed to various cryolitic-based environments, simulating the changes in bath chemistry beneath the cathode. The penetration and corrosion results were correlated with the testing parameters, the refractories' chemistry and microstructure as well as with the changes in reacted bath chemistry during penetration.

10:45 AM
Aging of Cathode Refractory Materials in Aluminium Reduction Cells: *Rikke Weibel*[1]; Leo Fisher Juhl[1]; Bent Nielsen[1]; Joergen Mikkelsen[1]; Ole-Jacob Siljan[2]; Kjeld Thovsen[2]; Sara Thornblad Mathisen[2]; [1]Skamol, Oestergade 58-60, Nykoebing DK-7900 Denmark; [2]Hydro Aluminium, Rsrch. Ctr. Porsgrunn, PO Box 2560, Porsgrunn N-3901 Norway

Aging of refractory materials during cell life has been studied in respect to changes in thermal conductivity and consequently influence on the heat balances. Autopsies have been performed on electrolytic cells with ages ranging from 500 days to 3200 days. Samples from different positions and layers in the cells, and of three different insulating materials are represented. Thermal conductivity measurements of the small autopsy samples have been performed by the Hot Disk method. During operation of the reduction cells the thermal conductivity of the pot lining material may change substantially (according to position in the cell, which is related to the degree of compression, precipitation of solids in pores, etc.) The physical properties of the virgin material (density, porosity, compressibility, etc.) also influences on the changes in thermal conductivity. The measured general increase in thermal conductivity of "spent" pot lining materials compared with similar virgin materials reflects the necessity of increasing cell voltage gradually during cell life in order to compensate for increased heat loss. Modelling of heat balances have been based on the thermal conductivity measurements on autopsy samples from three different ways of insulating the cathode construction, comparing two grades of moler bricks (HIPOR and SUPRA) with a combination of calcium silicate (SUPER-1100 E) and moler bricks (SUPRA). Heat balance modelling has showed that the lowest possible thermal conductivity of the insulating material is not the only important factor, also the evolution of the thermal conductivity over time is important (SUPER-1100 E versus HIPOR versus SUPRA).

11:10 AM
Environmental and Economic Aspects of an Effective Diffusion Barrier: *E. Sturm*[1]; J. Prepeneit[1]; [1]Hamburger Aluminium-Werk GmbH, Hamburg 21129 Germany

In pot lining there is a long history of more or less effective diffusion barriers. Some aspects of SPL, the need of reusing materials and further lowering of energy consumption has to be regarded. At HAW a double layer barrier in combination with alumina insulation has been experimented over more than 2000 days. The influence on heat balance has to be taken into account within a total lining concept, that includes cathode type and pot shell changes. The energy saving derives from a decrease in pot voltage of 50 mV. The mass balance of bath additives, impurities and fluorid is changed. Due to bath production there is a demand for low content of Na20 in alumina. Waste dumping of lining materials using alumina as insulation can be reduced. The cost balance of all the previous aspects reveals an economic solution.

11:35 AM
Aluminum-Steel Electrical Transition Joints, Effects of Temperature and Time upon Performance: *John G. Banker*[1]; Antoine Nobili[2]; [1]Dynamic Materials Corporation, Clad Metal Div., 5405 Spine Rd., Boulder, CO 80301 USA; [2]Dynamic Materials Corporation, Nobelclad Div., 1 Allee Alfred Nobel, Rivesaltes, 66600 France

Aluminum-steel electric transition joints (ETJ) are often used in aluminum and magnesium reduction cells for making welds between aluminum buss and steel anodes and cathodes. Depending upon the cell design and operation, ETJ's can operate at temperatures ranging between 200°C and 500°C, possibly hotter. Over time, these thermal conditions can have significant deleterious effect upon the ETJ bond strength, resulting in eventual failure. A detailed study was performed measuring ETJ bond strength as a function of time, temperature, and design. Specimens were maintained at temperatures of 300°C to 600°C for up to one year, and then tensile tests were performed. Metallographic and spectrographic analyses were performed to analyze the mechanism of bond degradation. Diffusion and subsequent intermetallic formation were the mechanisms causing bond degradation. Theoretical diffusion equations provide a basis for extrapolation of test data to longer time periods. The addition of a thin interlayer between the aluminum and steel can alter this behavior. Several interlayer materials were evaluated, including chromium and titanium. Titanium provided the most significant improvement in performance. Extrapolations indicate that titanium interlayer ETJ's can be expected to operate for over 10 years at 450°C without significant degradation.

Cast Shop Technology: Metal Treatment

Sponsored by: Light Metals Division, Aluminum Committee
Program Organizers: David H. DeYoung, Alcoa Technical Center, Alcoa Center, PA 15069 USA; John F. Grandfield, CSIRO Australia, Preston, Victoria 3072 Australia; Wolfgang Schneider, VAW Aluminium AG, Research & Development Manager Cast Technology, Bonn 53177 Germany

Wednesday AM — Room: 6A
February 20, 2002 — Location: Washington State Conv. & Trade Center

Session Chairs: Michael Scherbak, Alcoa Inc., Ingot Tech., 900 S. Gay St., Riverview Tower, Knoxville, TN 37902 USA; Masood Al-Rais, Dubai Aluminium, Techl. Services, PO Box 3627, Dubai UAE

8:30 AM Keynote
A Technical Perspective of Molten Aluminum Processing: *Peter D. Waite*[1]; [1]Alcan International, Ltd., Arvida R&D Ctr., 1955 Mellon Blvd., PO Box 1250, Jonquiere, Quebec G7S 4K8 Canada

In today's context of global competitiveness, all factors related to molten metal treatment which directly or indirectly affect product quality, the environment and processing costs, must be optimized. In this regard, technology and innovation play a decisive role for the development and implementation of the most appropriate molten metal treatment processes and practices. The following discussion will review the most recent significant developments in the field of molten aluminum processing, and outline potential areas for improvement.

9:00 AM
Investigation of the Process Variables Influencing Particulate Generation from Aluminum In-Line Metal Treatment Units: *Kevin A. Kitzman*[1]; [1]Alcoa, Inc., Environml. Sci. & Tech. Dvpt., Alcoa Technical Ctr., 100 Technical Dr., Alcoa Center, PA 15069-0001 USA

Maximum Achievable Control Technology (MACT) standards under the Clean Air Act set tough new limits on particulate and hydrogen chloride emissions from aluminum in-line degassing units that utilize chlorine. It is desirable to comply with these limits through process adjustments and/or redesign rather than through expensive end-of-pipe controls. Emissions sampling of five (5) types of in-line degassing technologies (3 vendor and 2 internal models) was conducted at various Alcoa plants under actual operating conditions to collect data on emission rates and process parameters. Emission results are presented against several operational factors to determine the factors that most significantly impact emissions. The most dramatic reduction in particulate emissions occurs by sealing the headspace above the metal, thereby preventing ambient air from entering. The impact of other significant process parameters on emissions is also discussed.

9:25 AM
Hycast I-60 SIR-A New Generation Inline Melt Refining System: *Geir Mæland*[1]; Erling Myrbostad[1]; Karl Venås[2]; [1]Hydro Aluminium, Hycast a.s., Industriveien 49, Sunndalsøra 6600 Norway; [2]Sør-Trøndelag University College, Trondheim Norway

A new generation inline melt refining unit has recently been developed by Hydro Aluminium, Hycast a.s. A traditional gas fluxing principle combined with a unique design, gives optimal utilization of the fluxing gas, and eliminates some of the disadvantages of the conventional degassing systems available today. The unit is characterized by very high removal of Hydrogen and inclusions. The operational costs are low. This is due to very low Argon gas consumption, a cheap preheating system, a drainfree reactor and relatively few rotors in operation. A two rotor system has a capacity of more than 65 metric tons pr. hour. The system is fully automated.

9:50 AM
A Radioscopic Technique to Observe Bubbles in Liquid Aluminium: Marc Bertherat[1]; Thierry Odievre[2]; *Michel P. Allibert*[1]; Pierre Le Brun[2]; [1]INP Grenoble, LTPCM, ENSEEG, BP75, St Martin d'Heres 38402 France; [2]Pechiney Centre de Recherches de Voreppe, 725 rue Aristide Berges, BP 27, Voreppe, Cedex 38341 France

A real time radioscopic visualization technique was used to observe the shape and motion of argon bubbles in liquid aluminium. The images provided by an X-ray generator on a radiographic screen were recorded and treated to extract the width and velocity of the bubbles. The treatment was validated by observations, at room temperature, of hollow spheres machined in a rotating aluminium block. The size and the velocity of bubbles were measured in a parallelipipedic graphite crucible where the bubbles could flow up without interactions with the crucible walls.

10:15 AM Break

10:30 AM
Hydrogen Removal Efficiency of In-Line Degassing Units: *Pierre Le Brun*[1]; [1]Pechiney Centre de Recherches de Voreppe, 725, rue Aristide Berges, BP27, Voreppe, Cedex 38341 France

The performance of in-line degassing units is often characterized by its hydrogen removal efficiency, defined by (hydrogen in-hydrogen out)/hydrogen in. This efficiency value has gained a wide acceptance as it is easy to define, understand, and measure, and is expected to be constant. Nevertheless, the meaning of the efficiency of a degassing unit is not often discussed. In this paper, we report on industrial experience, lab-scale experiments, and modeling in order to provide a better understanding of the factors that govern the degassing efficiency of an in line unit. We illustrate, among others, the influence of the following parameters: up-stream quality, casting parameters, control of the equipment, and external parameters. The benefits of a numerical hydrodynamic modeling approach are also illustrated.

10:55 AM
Methods for Alkaline Reduction: Either in the Potroom Crucible or in the Casthouse?: *Martin Bradley Taylor*[1]; [1]Stas, 1846 Outarde, Chicoutimi, Quebec G7K IHI Canada

Lithium, sodium, calcium and magnesium may all be reduced efficiently from molten aluminium to very low levels of ppm, in the pot room crucible before transfer to the melter/holder furnace and this within a few minutes; no chlorine is required, only the use of aluminium fluoride salt. Some removal, particularly of sodium, may also be obtained by simply transferring from one crucible to another whilst transporting or delivering molten aluminium, without the introduction of either gas or salt. On the other hand these same elements may also be reduced in the holder furnace in the casthouse, using either salts or gases by various means including manual additions of fluxes; or chlorine lances; or more recently rotary gas/flux injectors. Degassers may also be used as in-line treatment for removing alkalines with the use of argon and chlorine.

11:20 AM
Solubility of Carbon in Aluminium and its Effect upon the Casting Process: *John Rødseth*[1]; Bjørn Rasch[2]; Ole Lund[3]; Jomar Thonstad[4]; [1]Hydro Aluminium, R&D Matls. Tech., Håvik N-4250 Norway; [2]Hydro Aluminium, R&D Matls. Tech., Sunndalsøra N-6601 Norway; [3]Hydro Aluminium, Høyanger Metallverk, Høyanger N-5901 Norway; [4]Norwegian University of Science and Technology, Dept. Matls. Tech. & Electrochem., Trondheim N-7491 Norway

Carbon is slightly soluble in liquid aluminium (ppm range), the solid phase being aluminium carbide (Al_4C_3). The solubility of carbon in aluminium was determined experimentally, and the content of carbon in the aluminium was monitored on its way from the production cells to the casting line. Periodically the casthouse is plagued with metal that appears to be sticky and rapidly causes clogging of casting nozzles and filters in the casting line. This kind of metal, having no official name, is often called "summer metal" or "blue metal". The amount of aluminium carbide is closely connected to the occurrence of "blue metal", being particularly critical for continuous casting processes like rod casting and strip casting. The paper focuses on the level of carbon in the electrolysis cells and the formation and removal of aluminium carbide in the casting process.

11:45 AM
Assessment of the Hydrogen Level in 319 Aluminum Alloy Melts using the Thermal Analysis Technique: *M. Djurdjevic*[1]; R. Hasenbusch[2]; J. H. Sokolowski[1]; [1]NSERC/Ford-Nemak/University of Windsor Industrial Research Chair, Mechl., Autom. & Matls. Eng., Rm. 203, Essex Hall, 401 Sunset Ave., Windsor, Ontario N9B 3P4 Canada; [2]Nemak Corporation of Canada, Casting Process Dvlp. Ctr., 4655 G. N. Booth Dr., Windsor, Ontario N9C 4G5 Canada

One of the major problems associated with cast aluminum components is the formation of porosity. Porosity is a leading cause in the reduction of mechanical properties, loss of pressure tightness and a degradation of the surface appearance in cast components. Porosity formation is generally attributed to shrinkage coupled with a lack of interdendritic feeding during the mushy zone solidification and evolution of hydrogen bubbles due to a sudden decrease in hydrogen solubility during the solidification process. This paper presents the results of studies aimed at developing a new procedure for on-line assessment of hydrogen levels in 319 aluminum melts using the Aluminum Thermal Analysis System (AlTAS). The results of the statistical correlation between characteristics of the cooling curve, melt temperature and chemistry indicate that the level of dissolved hydrogen (as measured by the AlSCAN unit) can be determined by the AlTAS system with R2 = 0.82 predictability.

Charles J. McMahon Interfacial Segregation and Embrittlement Symposium: New Methods for Study of Segregation and Fracture II

Sponsored by: ASM International: Materials Science Critical Technology Sector, Structural Materials Division, Materials Processing & Manufacturing Division, Jt. Mechanical Behavior of Materials, Jt. Computational Materials Science & Engineering, Texture & Anisotropy Committee
Program Organizers: Vaclav Vitek, University of Pennsylvania, Department of Materials Science and Engineering, Philadelphia, PA 19104 USA; Clyde Briant, Brown University, Division of Engineering, Providence, RI 02912 USA; Harvey D. Solomon, General Electric Company, Research & Development Center, Schenectady, NY 12309 USA

Wednesday AM	Room: 307-308
February 20, 2002	Location: Washington State Conv. & Trade Center

Session Chairs: Hiroo Ohtani, Sumitomo Metal Industries, Corporate Rsrch. Labs., 1-8 Fuso-cho, Amagasaki Japan 660-0891; Christian Elsässer, Max-Planck-Institut für Metallforschung, Institut für Werkstoffwissenschaft, Seestrasse 92, D-70174 Stuttgart Germany

8:30 AM Invited
The Relationship Between the Onset of Plastic Flow in Nearly Perfect Silicon Samples and the Brittle to Ductile Transition: *David P. Pope*[1]; M. Khantha[1]; Robert H. Folk[1]; Vaclav Vitek[1]; [1]University of Pennsylvania, Matl. Sci. & Eng., lrsm Bldg., 3231 Walnut St., Philadelphia, PA 19104 USA

Nearly perfect single crystalline Si wafers have been extensively used in the past ten years to study dislocation activity at the BDTT because the absence of pre-existing dislocations in these samples means that all dislocations are generated at the transition. However to date, most of the experiments have been conducted on notched or pre-cracked samples because it is widely believed that the BDT results from some type of crack-tip phenomenon. We believe that the BDT occurs when a critical combination of stress and temperature results in the generation of an avalanche of dislocations in the material, permitting general yielding. In this view, a crack-tip is not necessary for the transition but it may serve as the stress concentrator that precipitates the avalanche of dislocations. To test this hypothesis, experiments were performed on a large number of dislocation free, notch free silicon specimens, produced using photolithography. These silicon beams were tested in bending at various elevated temperatures and strain-rates and reveal a strain-rate dependent brittle-to-ductile transition in these defect-free samples. Dislocation etch-pit analysis of the sample surfaces show that massive dislocation activity occurs prior to yielding in the highest stressed portions of the beam. In addition, the scanning electron microscope images reveal a qualitative increase in dislocation activity above the BDTT, in agreement with the observed upper yield point behavior. The Khantha-Pope-Vitek model of the BDT is proposed to address these new observations.

9:05 AM Invited
Effects of Segregation in Cu and Ni3Al upon Impact Fracture: An Ultra-High Vacuum Study with Local Probe Scanning Auger/Scanning Electron Microscopy: *Jeff Th. De Hosson*[1]; D. van Agterveld[1]; G. Palasantzas[1]; [1]University of Groningen, Dept. of Appl. Phys., Nijenborgh 4, Groningen 9747 AG The Netherlands

This contribution deals with applications of UHV-local probe scanning Auger/scanning electron microscopy to the field of segregation. Results will be discussed of two different systems: Cu-S and Ni3Al-B materials. In-situ fracture of copper-alloys containing copper-sulfide precipitates exhibits areas in the form of pits. The wide variety of morphologies depends significantly on the size of the existing precipitate. As a second example B-doped polycrystalline Ni3Al (~0.1-0.5 % at. B) is chosen. In particular this contribution concentrates on phenomena of the electron beam induced oxidation of surfaces of Ni3Al-base alloys. It appears that an electron beam may contribute substantially to the oxidation behavior of polycrystalline and Ni3Al-B surfaces during Auger analysis at room temperature. Therefore special care should be taken in Boron segregation studies onto Ni3Al-B surfaces/interfaces with Auger microscopy because of irreversibly structural changes associated with an intense Ni-oxide formation by the electron beam.

9:40 AM
Segregation in PdO/Pd Alloy Systems: Matthew Augustine[1]; Heng Zhang[1]; *Harris L. Marcus*[1]; [1]University of Connecticut, Inst. of Matls. Sci., Storrs, CT 06269-3136 USA

PdO is a major catalyst for low temperature combustion of natural gas. This paper will describe research efforts on the nature of surface segregation of alloying elements in Pd and PdO and relate them to the catalytic behavior. The high temperature surface analysis was performed in-situ in both a scanning Auger spectrometer and an XPS system.

10:00 AM
Effect of Solutes on Grain Boundary Sliding in Aluminum: *J. S. Vetrano*[1]; C. H. Henager[1]; R. J. Kurtz[1]; R. G. Hoagland[1]; V. Gertsman[1]; [1]Pacific Northwest National Laboratory, Richland, WA 99352 USA

We have used mechanical testing, microstructural evaluation and computational studies to elucidate the role of magnesium and tin on grain boundary dislocations (GBD) and grain boundary sliding (GBS) in aluminum. Whereas in some instances solute segregation can be detrimental to properties, enhanced sliding caused by segregation can be beneficial to forming operations such as superplastic deformation. Mechanical testing has revealed that magnesium segregates to grain boundaries during sliding and tin can either enhance or reduce the superplastic elongation. Microstructural studies in the transmission electron microscope have shown that tin resides along grain boundaries and particularly triple points so its effect is localized. Further studies are being carried out to further understand how tin is affecting the deformation. Computational studies on an aluminum symmetric tilt grain boundary performed using embedded atom method techniques showed that sliding resistance increased with increasing concentration of magnesium. Atomistic studies also revealed that magnesium segregation inhibited core spreading of GBDs thereby decreasing their mobility. These studies are working to better elucidate how solutes effect the structure and properties of grain boundaries. Work supported by the Materials Science Division, Office of Basic Energy Sciences, US Department of Energy under contract DE-AC06-76RLO-1830.

10:20 AM
Surface Segregation in an Al-4.2At%Ag Alloy: *Robert W. Hyland*[1]; H. K. Lee[2]; H. I. Aaronson[3]; P. P. Wynblatt[3]; [1]KB Alloys, Inc., R&D/Tech., 220 Old W. Penn Ave., Box 53, Robesonia, PA 19551 USA; [2]International Business Machines Corporation, Gen. Tech. Div., Essex Junction, VT 05452 USA; [3]Carnegie Mellon University, MSE, Pittsburgh, PA 15213 USA

The equilibrium surface composition of a polycrystalline Al-4.2 at%Ag alloy has been measured as a function of temperature using Auger electron spectroscopy. Results indicate that silver segregates to surfaces with an apparent enthalpy of segregation of about -38 kJ/mol. The equilibrium average surface composition of the alloy has been calculated as a function of surface orientation using the Lee-Aaronson discrete lattice plane model. A modified regular solution model originally due to Alexander et al. was used to represent the interactions between Al and Ag. While this method successfully described the bulk thermodynamic properties of Al-Ag, it predicted no surface segregation of Ag. Possible reasons for the disagreement are considered. Finally, the surface segregation of silver measured by AES was compared with that predicted by the Gibbs adsorption isotherm, wherein the latter calculation made use of results of ultra high vacuum measurements of the bulk composition dependence of the surface tension of α Al-Ag alloys. Qualitative agreement was found between the two experimental methods, both indicating enrichment of Ag at the free surfaces.

10:40 AM
The Effect of Impurities on Phase Transformation Kinetics: *Robert C. Pond*[1]; Steven Celotto[1]; [1]University of Liverpool, Dept. of Eng., Matls. Sci. & Eng., Brownlow Hill, Liverpool L69 3BX UK

The principal thrust of our recent work has been to establish a mechanistic model of martensitic transformation that is consistent with the phenomenological theory of martensite crystallography (PTMC). This has been achieved in terms of a mechanism involving transformation dislocations moving along the parent-martensite interface and lattice-invariant deformation (LID) generated in the martensite. Modelling the transformation process in this way gives a deeper insight into the central proposition of the PTMC, i.e. the existence of an invariant plane in the shape deformation. This approach demonstrates that very special crystallographic circumstances must prevail for a transformation process to be diffusionless. For example, diffusional accommodation will be required if an appropriate mode of LID is activated or when the transformation interface interacts with defects in the parent phase. As a consequence, the rate of transformation will be much slower. The aim of the present paper is to discuss the effect of impurities in transformation kinetics through their influence in the activated mode of LID and the motion of transformation dislocations.

11:00 AM
Segregation, Ordering Effects and Relaxations at Surfaces and Interfaces of the Cu-Au System: *Hariton Michael Polatoglou*[1]; Anthoula Maidou[1]; [1]Aristotle University of Thessaloniki, Phys. Dept., Gr-54006 Thessaloniki Greece

An N-body potential semi-empirical tight binding model in the second moment approximation is used to describe the atomic interactions of the Cu-Au system, that allows the study of dynamical properties of the ensemble. The parameters are determined from T=0K structural data and elastic properties of Cu, Au and Cu3Au. Monte Carlo simulations in the constant temperature, pressure and chemical potential difference method are used to determine thermodynamic properties of the Cu-Au system of bulk, surfaces and interfaces of the intermetallic compounds, and for stoichiometries close to the intermetallic compounds of the system, for temperatures below and above the order-disorder transition temperature. After realistically reproducing the thermodynamic properties of the bulk intermetallic compounds, we investigate the surfaces and interfaces studying segregation phenomena and the ordering processes. Findings show different behavior for different geometries, i.e. strains present at the interfaces may produce ordering phenomena even for temperatures above Tc.

11:20 AM
Neutron Irradiation-Induced Non-Equilibrium Intergranular Segregation: Segregation Capability vs. Kinetics: *Jun Kameda*[1]; Yutaka Nishiyama[2]; Tamara E. Bloomer[3]; [1]Iowa State University, Ames Lab., Ames, IA 50011 USA; [2]Japan Atomic Energy Research Institute, Tokai, Ibaraki 319 Japan; [3]US Nuclear Regulatory Commission, Washington, DC 20555 USA

Non-equilibrium intergranular segregation induced by neutron irradiation and post-irradiation annealing (PIA) has been studied in several model ferritic alloys doped with phosphorus, manganese and/or copper. Irradiation-induced phosphorus segregation became more prominent with decreasing bulk phosphorus content. A PIA study has shown that the phosphorus segregation proceeds at lower PIA temperatures via mobile phosphorus-interstitial complexes while phosphorus desegregation dominates due to vacancy/phosphorus exchange during PIA at higher temperatures and/or for prolonged time. Correlation between the changes in segregated phosphorus and hardness, which is related to phosphorus rich precipitates, is presented. The mechanisms of non-equilibrium intergranular segregation during neutron irradiation are discussed in light of coupled fluxes of point defects and phosphorus, and the segregation capacity of grain boundaries to absorb to phosphorus. This work was supported by the USDOE. Office of Basic Energy Sciences, Division of Materials Sciences.

11:40 AM

Temperature and Stoichiometry Effects on Grain Boundary Structure and Cohesion in NiAl: Xuepeng Xie[1]; *Yuri Mishin*[1]; [1]George Mason University, Sch. of Computl. Scis., 4400 University Dr., MSN 5C3, Fairfax, VA 22030 USA

The equilibrium atomic structure of several symmetrical tilt grain boundaries in the B2-ordered intermetallic compound NiAl is studied using Metropolis Monte Carlo simulations and the embedded-atom method. At high temperatures, the grain boundaries tend to be enriched in Ni relative to the stoichiometric or Ni-rich lattice. In most cases the Ni segregation takes place by the substitution of Al atoms by Ni atoms without changing the boundary structure. In some boundaries, however, the Ni segregation alters the initial boundary structure (structural transformation). In Ni-rich alloys, the structure of some boundaries becomes virtually disordered. The impact of these effects on the reversible work of decohesion and cohesive strength of grain boundaries is evaluated.

Commercial Mini-Sessions

Sponsored by: Light Metals Division,
Program Organizers: David V. Neff, Metaullics Systems Company, Solon, OH 44139 USA; Wolfgang Schneider, VAW Aluminium AG, Research & Development Manager Cast Technology, Bonn 53177 Germany

Wednesday AM — Room: 401
February 20, 2002 — Location: Washington State Conv. & Trade Center

Session Chair: David V. Neff, Metaullics Systems Company, 31935 Aurora Rd., Solon, OH 44139 USA

Computational Modeling of Materials, Minerals & Metals Processing: Wednesday AM Plenary Session 9:00 AM – 9:45 AM

Sponsored by: Materials Processing & Manufacturing Division,
Program Organizer: Mark Cross, The University of Greenwich, Centre for Numerical Modelling and Process Analysis, Old Royal Naval College, 30 Park Row, Greenwich, London SE10 9LS UK

Wednesday AM — Room: 619-620
February 20, 2002 — Location: Washington State Conv. & Trade Center

Session Chairs: Mark Sammonds, UES Software, Inc., 175 Admiral Cochran Dr., Annapolis, MD 21401 USA

Keynote

Micro-Macro Modeling of Solidification Processes and Phenomena:*Vaughan Voller*[1]; [1]University of Minnesota, 500 Pillsbury Dr., Minneapolis, MN 55455 USA

The wide range of length and time scales found in solidification processes are outlined and discussed. Methods for Direct Microstructure Simulation (DMS) are introduced. Key features in sharp interface and phase field models are presented. Concepts in micro-macro solidification modeling are covered. Basic details of microstructure and segregation models are provided. A description of a recent segregation micro-macro model is presented in detail.

Computational Modeling of Materials, Minerals & Metals Processing: Track A - Heat & Mass Transfer - II

Sponsored by: Materials Processing & Manufacturing Division,
Program Organizer: Mark Cross, The University of Greenwich, Centre for Numerical Modelling and Process Analysis, Old Royal Naval College, 30 Park Row, Greenwich, London SE10 9LS UK

Wednesday AM — Room: 619
February 20, 2002 — Location: Washington State Conv. & Trade Center

Session Chairs: Thomas Battle, DuPont Company, White Pigment & Minl. Production, Edgemoor Plant, 104 Hay Rd., Edgemoor, DE 19809 USA; Rod Guthrie, McGill Metals Processing Center, 3610 University St., MH Wong Bldg., Rm. 2MO51, Montreal, Quebec, H3A 2B2 Canada

9:45 AM

A Steady State Electrothermic Simulation Analysis of a Carbothermic Reduction Reactor for the Production of Aluminium:*Dimitrios I. Gerogiorgis*[1]; B. Erik Ydstie[1]; Sridhar S. Seetharaman[2]; [1]Carnegie Mellon University, Dept. of Cheml. Eng., 5000 Forbes Ave., Pittsburgh, PA 15213 USA; [2]Carnegie Mellon University, Dept. of Matls. Sci. & Eng., 5000 Forbes Ave., Pittsburgh, PA 15213 USA

Carbothermic reduction is an important process alternative for aluminium production, based on the endothermic chemical reduction reaction occurring between aluminium oxide and carbon. This process has potential for drastic reduction of fixed and operational costs of the investment. Furthermore, it is environmentally benign and in principle significantly more energy-efficient, as the costly electrolytic ionization is effectively avoided by direct chemical reduction. Carbon monoxide production can contribute to the energy integration of the process, as the installation of a conjugate power cycle allows for production of electric energy necessary for heating purposes. The carbothermic production of aluminium can occur in a two-stage high-temperature reactor. Carbon and aluminium oxide pellets are introduced into an electric arc furnace (1st stage) and undergo melting at a temperature of ca. 1950°C, thus forming a high-temperature molten slag. This multicomponent molten slag (carbon, aluminium oxide and carbide, carbon monoxide) is fed to a subsequent 2nd stage, where it reacts at a higher temperature (2050°C) to aluminium. The 2nd stage reaction products (carbon monoxide, molten pure aluminium) are then separated. The present study focuses on a Computational Fluid Dynamics (CFD) simulation of the flowfield within the carbothermic reduction reactor, which is an essential step for the effective conceptual design of pilot and production plants. This CFD simulation of the melt flow encompasses important research challenges, due to the limited knowledge of thermophysical properties for high-temperature multicomponent molten slags and the significant experimental limitations. The computational domain for the CFD simulation is defined as a rectangular sector, while the computational expense of the simulation can be minimized by considering symmetry planes. The CFD model for computation adopts simplifying assumptions for production (Joule effect) and consumption (endothermic reaction) of heat, considering a pseudohomogeneous molten slag. The CFD simulation is performed in a hexahedral structured grid (selecting uniform meshing) using a commercially available CFD code (CFX 4.3-AEA) with some necessary modifications. The main objective of the present CFD simulation study is to extract conclusions regarding the design of a carbothermic reactor and also understand how process parameters affect this system.

10:10 AM

The Limitations of CFD Modelling for Furnace Atmosphere Troubleshooting:*Paul F. Stratton*[1]; Neeraj Saxena[2]; M. Huggahalli[2]; [1]BOC Gases, European Dvlp. Ctr., Rother Valley Way, Holbrook, Sheffield, SY S20 3RP UK; [2]BOC Gases R&D, 100 Mountain Ave., Murray Hill, NJ USA

Furnace temperatures and atmospheres are the most important factors in an industrial heat treating processes. To create an atmosphere in a continuous furnace, several gases, either singly or as mixtures, are used. These include nitrogen, hydrogen, exothermic and endothermic atmospheres, natural gas, propane and cracked methanol. Which gas or gases and how much of each should be used in the furnace is largely based on experience or on expensive trial and error experiments. BOC Gases has developed a simplified, easy-to-use PC based model to facilitate the understanding, troubleshooting and design of atmosphere injection into heat treating furnaces and to minimise wasteful experimentation. The model takes into account the role of oxygen, nitrogen, hydrogen, methane, carbon monoxide, carbon dioxide and water vapour in the heat treating process. Fundamental energy and mass conservation equations are solved to determine atmosphere profiles in a furnace for given compositions of gases injected. The reducing and carburising potentials of the gases, necessary to design any heat treating process, can be deduced using this model. The model can also be used to design and troubleshoot the atmosphere injection practice. Using model simulations, the critical process variables can be identified and the heat treating process optimised using a minimal number of experiments on the production floor. To validate the model industrial examples are examined. The results of this model were found to compare quite well with actual data obtained from production furnaces.

10:35 AM Break

10:50 AM
Simulation of Internal Oxidation: *Henrik Larsson*[1]; Martin Schwind[1]; John Ågren[1]; [1]Royal Institute of Technology, Matls. Sci. & Eng., Stockholm SE-100 44 Sweden

Internal oxidation is simulated in three dimensions using a combined random walk-cellular automata approach. Nucleation theory is used for the early stages of growth. Diffusion is modelled utilising discrete units, whereby a transformed Fick-Onsager law is solved by a simple stochastic method. Growth and dissolution of precipitates are treated by applying the local equilibrium hypothesis and the Gibbs-Thomson equation. Grain boundaries are included in the model; their effect on diffusion, nucleation and growth are taken into account.

11:15 AM
Dynamic Model for a Vapor Recovery in Carbo-Thermic Aluminum Process: *Vianey Garcia-Osorio*[1]; Tor Lindstad[2]; B. Erik Ydstie[1]; [1]Carnegie Mellon University, Cheml. Eng., 5000 Forbes Ave., Pittsburgh, PA 15213 USA; [2]SINTEF, Matls. Tech., Alfred Getz vei 2, Trondheim N-7465 Norway

As a result of the high temperatures present in a Carbothermic Aluminum Process the content of aluminum and aluminum sub oxide in the gases leaving this process is high. These gases must be recovered. For this purpose a Vapor Recovery Unit is introduced in the system. Inside this unit the aluminum compounds react in a series of heterogeneous non-catalytic reactions forming solid, liquid and gas products. The different product phases depend on the temperature present in the system. Therefore the model needs to capture the physics of the system and accurately represents the interaction between the energy and material balances and process thermodynamics. In this work a dynamic model of the Vapor Recovery Unit is presented. Because of the complexity of the system several models are developed and coupled to capture the essential physics of the multiphase reaction problem. A shrinking core model is used to describe the reaction mechanisms. Then material and energy balances are coupled with the thermodynamic properties from the FACT database of physical properties, resulting in a system of nonlinear Partial Differential Equations. In the paper we describe the model development and governing equations for the reaction mechanisms and fluid flow. Finally we review the numerical schemes created for the solution of the model system. The model can be used for control and design purposes.

11:40 AM
Computer Simulation of the Structure-Energetical Transformations at Combustion Synthesis in the Systems NiAl and TiAl: *Mikhail D. Starostenkov*[1]; Gennadiy M. Poletayev[1]; Alexandra S. Starostenkova[1]; [1]Altai State Technical University, Gen. Phys. Dept., 46 Lenina Pr., Barnaul, Altai Region 656099 Russia

It is known, that combustion synthesis (CS) takes place at high velocities. That is why it is difficult to determine the stages of structure-energetical transformations, taking place at CS. The process of CS is modelled by the computer simulation, using molecular dynamics method. The investigating systems are presented in a form of bimetal thin films at the beginning of the process. The interactions between the atoms are given by the sets of emperic pair potentials. The set of critical parameters, regulating the velocity of the reaction of CS is found in the result of computer experiment. The parameters are the following: limited free volume, its connection with the temperature of the process beginning, the velocity of components mixing, the velocity of formation of intermetallic phases. It is established, that the structure transformations of the system take place at the formation of nanocrystal phases in the process of CS. Character of structure-energetical transformation at combustion synthesis in the systems NiAl and TiAl depend from the orientation of contacting plains in bimetal thin films.

12:05 AM
Influence of Surface Pressure and Slag Layer on Bubble Bursting in Degasser Systems: *Julie Cranga*[1]; Pascal Gardin[1]; Didier Huin[1]; Jacques Magnaudet[2]; [1]IRSID, THEMEF, Voie Romaine, BP30320, Maizieres les Metz 57283 France; [2]IMFT, Groupe Interface, Allee du Professeur Camille Soula, Toulouse 31400 France

For the control of steel grade in steelmaking reactors, IRSID and IMFT are building a new modelling of bubble behavior in the vicinity of liquid steel/slag interface. The objective is to identify the main parameters affecting hydrodynamics of the different phases and to supply the mass transfer models commonly used at IRSID with the appropriate fluid mechanic parameters (local velocities, bubble residence time in the melt ...). Special emphasis is given to the study of pressure influence on bubble bursting. The topics of the paper are: *First to describe the numerical VOF method developed to predict the multiphase flow including bubbles, liquid metal and slag layer. *Second to analyze the influence of pressure in RH degasser on bubble bursting. Validation is given by comparison with previous results in literature. The major point concerns the distinct behavior whether the pressure is low or high. *Third to study the influence of slag layer on liquid metal entrainment in the wake of the bubble and on the nature of projection from the bath surface, in relation with the slag layer thickness and physical properties (viscosity and interfacial tension).

Computational Modeling of Materials, Minerals & Metals Processing: Track B - Melting & Solidification - III

Sponsored by: Materials Processing & Manufacturing Division,
Program Organizer: Mark Cross, The University of Greenwich, Centre for Numerical Modelling and Process Analysis, Old Royal Naval College, 30 Park Row, Greenwich, London SE10 9LS UK

Wednesday AM	Room: 620
February 20, 2002	Location: Washington State Conv. & Trade Center

Session Chairs: Mark Samonds, UES Software Inc., 175 Admiral Cochran Dr., Annapolis, MD 21401 USA; Srinath Viswanathan, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6083 USA

9:45 AM
Computational Studies of the Control of Convection in Diamagnetic Liquids during Solidification with Magnetic Field Gradient: *C. B. Seybert*[1]; J. W. Evans[1]; [1]University of California, Dept. of Matls. Sci. & Eng., Berkeley, CA 94720 USA

Natural convection is a commonplace phenomenon in the solidification of materials. Driven by temperature gradients, concentration gradients or both, it plays a role in the development of macrosegregation and the microstructure of the solid. The paper describes an investigation, both by experiment and by mathematical modeling, into this natural convection and whether it can be controlled by the application of a magnetic body force. This force is not the Lorenz force, that can be used to damp convection in conducting fluids, but the magnetic body force that arises from a gradient in the magnetic field. If that gradient is of the right size and direction it can be made to eliminate buoyancy or even to levitate a fluid. The experimental investigation has entailed the measurement of velocities and solidification front positions in transparent liquids, with PIV used for the former. The measurements have been carried out for water and aqueous solutions of manganese chloride. In the latter case most of the measurements have been made with the solution in the bore of a superconducting magnet at Marshall Space Flight Center and it has been demonstrated that natural convection in this paramagnetic solution can be greatly reduced, perhaps halted, by the magnetic field. Measurements agree reasonably well with computations performed using FLUENT and this CFD package has been used to predict the conditions under which natural convection within a diamagnetic fluid might be halted.

10:10 AM
Methods for Approximating Discontinuous or Rapidly Changing Conductivity in Numerical Calculations: *Vaughan Richard Voller*[1]; [1]University of Minnesota, Civ. Eng., 500 Pillsbury Dr. S.E., Minneapolis, MN 55455 USA

Much is said in the recent literature on the modeling necessity of obtaining appropriate thermo-physical properties; in particular the requirement to account for properties that are "strong" functions of the depended variables, e.g., temperature. Of course obtaining appropriate thermo-physical properties serves no purpose unless they can be accurately integrated into a discrete numerical calculation. The purpose of this paper is to examine how temperature dependent conductivities that exhibit discontinuities or rapid changes can be handled in a numerical code. A simple approach based on a local application of a Kirchoff transformation at the discrete level is presented. The application of this transformation–that does not require any inversion–is demonstrated on solving a range of one and two dimensional test problems.

10:35 AM Break

10:50 AM
Modelling of the De-Waxing of Investment Cast Shells: Jean-Christophe Gebelin[1]; Sam Jones[1]; *Mark R. Jolly*[1]; [1]The University of Birmingham, IRC in Matls., Edgbaston, Birmingham, W. Midlands B15 2TT UK

The de-waxing process in investment casting is truly a black art which is carried out in a black hole–the autoclave. The process involves exposing wax, coated by a porous ceramic shell, to steam at a pressure of 10 bar and a temperature of about 180°C. The process which then occur are truly multi-media and multi-physics. Steam condenses in the porous ceramic, wax melts and flows, the shells expand and sometimes crack. Why the shells crack is one of the most difficult questions asked in the industry. Modelling and validating the de-waxing process is not simple. The IRC at the University of Birmingham is attempting to model this process using Physica+ a code developed in the UK. This paper will present the latest results in the attempt to model one of the casting industries most intractable problems.

11:15 AM
The Swirling Effect in an Immersion Nozzle on the Flow in a Continuous Casting Mold: *Shinichiro Yokoya*[1]; Sigeo Takagi[1]; Manubu Iguchi[1]; Katsukiyo Marukawa[3]; Shigeta Hara[2]; [1]Nippon Institute of Technology, Mechl. Eng., 4-1 Miyashiro, Minami-saitama, Saitama 345-8501 Japan; [2]Osaka University, Dept. of Matls. Sci. & Proc., Yamadaoka, Suita, Osakafu 565-0000, Japan; [3]Osaka University, Sumitomo Metal Industries, Ltd., Japan

A numerical analysis and water model study of the mold region of a continuous casting apparatus are performed with a novel injection concept using swirling flow in the pouring tube, to control the heat and mass transfer in the continuous casting mold. As a result, the following results were found: (1)By changing swirl strength, it is easy to control the flow pattern as well as the direction of the flow. (2)Uniform velocity distribution can be obtained within a very short distance from the outlet of the nozzle. (3)Heat and mass transfer near the meniscus can be remarkably activated compared with a conventional straight type immersion nozzle without swirl. (4)Swirl helps the superheat in the melt dissipate. (5)Penetration depth of the nozzle outlet flow is decreased remarkably by the application of swirling. Those findings mentioned above are very useful to control the flow pattern in the continuous caster.

11:40 AM
Computational Modelling of Metals Extrusion and Forging Processes: *A. J. Williams*[1]; T. N. Croft[1]; M. Cross[1]; [1]University of Greenwich, Ctr. for Numl. Modlg. & Proc. Analy., The Old Royal Naval College, 30 Park Row, London SE10 9LS UK

The computational modelling of extrusion and forging processes is now well established. In this work a novel approach is described which utilises finite volume methods on unstructured meshes. This technique can be used to solve simultaneously for fluid flow, heat transfer and non-linear solid mechanics and their interactions. The approach involves the solution of free surface non-Newtonian fluid flow equations in an Eulerian context to track the behaviour of the workpiece and its extrusion/forging, and the solution of the solid mechanics equations in the Lagrangian context to predict the deformation/stress behaviour of the die. Some preliminary examples of this approach will be discussed.

12:05 PM
The Role of Orifice Shape in the Detection of Inclusions in Liquid Metals: *Roderick I.L. Guthrie*[1]; Mei Li[1]; [1]McGill Metals Processing Centre, Canada

A mathematical model was developed to study the role of orifice shape in the detection of inclusions in LiMCA (Liquid Metal Cleanliness Analyzer) system. The fluid flow field within the ESZ was obtained by solving the Navier-Stokes equations. The trajectories of entrained particles were calculated using the equations for motion of particles. A numerical study of the effect of orifice shape on signal shape generated by inclusions passing through orifice showed that the signals in a parabolic orifice are gaussian in shape, while those in a cylindrical orifice are trapezoidal in shape. This signal shape difference needs to be taken into account when performing particle discrimination. Orifice shape influences also pass-through fraction of inclusions. Finally, a study of the orifice shape on critical conditioning currents suggested that as the polynominal coefficient of the parabolic orifice increases, the critical conditioning current, which is also the maximum operating current, decreases dramatically. These critical conditioning currents also increase as the fluid flow velocity within the ESZ increases.

Computational Phase Transformations: Phase Equilibria from First Principles

Sponsored by: ASM International: Materials Science Critical Technology Sector, Electronic, Magnetic & Photonic Materials Division, Structural Materials Division, Chemistry & Physics of Materials Committee, Jt. Computational Materials Science & Engineering, Thermodynamics & Phase Equilibria Committee
Program Organizers: Long-Qing Chen, Pennsylvania State University, Materials Science and Engineering Department, University Park, PA 16802-5005 USA; Mark Asta, Northwestern University, Department of Materials Science and Engineering, Evanston, IL 60208-3108 USA; Zi-Kui Liu, Pennsylvania State University, Materials Science and Engineering, University Park, PA 16082-5005 USA; James Aaron Warren, NIST, CTCMS and Metallurgy Division, Gaithersburg, MD 20899-8554 USA

Wednesday AM — Room: 201
February 20, 2002 — Location: Washington State Conv. & Trade Center

Session Chair: Mark Asta, Northwestern University, Dept. of Matls. Sci. & Eng., 2225 N. Campus Dr., Evanston, IL 60208-3108 USA

8:30 AM
First-Principles Quantum Mechanical Predictions of Alloy Ground States and Microstructures: *Alex Zunger*[1]; [1]National Renewable Energy Laboratory, Golden, CO 80401 USA

There is a lot of talk of computer-aided discoveries/design of new materials, but the simple fact is that even limiting oneself to materials made of just two elements, (e.g., Cu-Au or Si-Ge), and to a substitutional system there can exist as many as 2^N configurations that include compounds, alloys, superlattices, and impurities. Indeed, even for a modest number of sites N, this is an astronomical number. Thus, the conventional energy minimization approach for selecting the most stable crystal structure for A_pB_q (e.g., first-principles pseudopotentials) is hopeless if one considers the full 2^N space configurations of A, B on a lattice of N points. Thus, contemporary energy minimization approaches use instead the method of "rounding-up the usual suspects": selecting the most stable from only a small number of well-known candidate structures. The potential for missing new and important structures is obviously large. Even if we know the stable structure at T=0, we need to further know how it looks at finite-temperatures. This requires modeling short-range-order (SRO), precipitate morphology, etc. Computationally, this could need "supercells" with 10^4-10^6 atoms. This talk outlines the approach to a solution. It addresses the questions of: (i) finding the lowest energy configuration of substitutional systems; (ii) calculating their composition-temperature phase diagram; and, (iii) their finite-temperature microstructure, including precipitate shapes and SRO, using the first-principles local density approximation (LDA). Mapping of the LDA energies of only 10-20 A_pB_q compounds onto an Ising-like "cluster expansion" enables use of lattice statistical mechanics techniques that elegantly solve the above problems. This extends the utility of the LDA from simple, perfectly-ordered compounds to truly complex structures. I will illustrate the method for semiconductor systems (GaAs-AlAs, GaAs-InAs, InP-GaP) and transition-metal intermetallic systems (Cu-Pd, Cu-Au, Ni-Pt, Ag-Pd, Cu-Zn, Ni-V, Ag-Au, Rh-Pt, Li_x• $_{1-x}CoO_2$, Sc_{1-x}• $_xS$), showing how previously unsuspected structures and materials are predicted, and how one can predict precipitate morphology.

9:15 AM
Electronic Structure Calculations of Random Alloys: A Step Towards a Modeling and Understanding of Phase Equilibria: *Igor Anatolievich Abrikosov*[1]; [1]Uppsala University, Phys. Dept., Ångströmlaboratoriet, Box 530, Uppsala SE-75121 Sweden

A state-of-the-art approach to the theoretical simulations of the phase stabilities includes a combination of first-principles electronic structure calculations with methods of atomic-scale simulations and statistical mechanics. In doing so one can treat extremely complex systems and processes with very high level of accuracy and reliability. In this regards, an ability to describe the electronic structure of random alloys has become an essential step towards a modeling and understanding of phase equilibria. We discuss recent developments of the methodological base in this field. We formulate the electronic structure problem for systems with or without translational symmetry completely in terms of Green's functions within a Linear Muffin-Tin Orbitals (LMTO) as well as within an Exact Muffin-Tin Orbitals (EMTO) basis sets. The calculations of the total energies, electronic structure, and effective interatomic interactions in different systems will be discussed, including fcc and hcp phases of Cu-Zn, random fcc Al-Zn alloys, two forms of cerium oxide, and magnetic semiconductors. The whole scheme of this multiscale modeling is illustrated by calculations of surface segregations in fcc Ni-Pt alloy.

9:45 AM

Ab Initio Study of One-Dimensional Long-Period Structures in Al3Ti, Cu3Pd, and Au3Zn Compounds: *Catherine Colinet*[1]; Alain Pasturel[2]; [1]LTPCM/ENSEEG, BP 75, Saint Martin d'Heres 38402 France; [2]Laboratoire de Physique numerique des Systèmes Complexes, Maison des Magisteres CNRS, BP 166, Grenoble, Cedex 38042 France

In a number of ordered face-centred cubic A3B compounds one-dimensional long-period structures (1D-LPS's) are observed experimentally. These superstructures are lattices based on L12 structure and may be viewed as periodic arrangements of (001) antiphase boundaries. We have performed ab initio calculations of the stability of 1D-LPS's in Al3Ti, Cu3Pd, and Au3Zn employing the Vienna ab initio simulation package (VASP). In each system the energetic effects due to the tetragonal distortion and of the cell-internal displacements of the atoms in the 1D-LPS's are studied. The effects are very important in the case of Al3Ti compound, and very small in the cases of Cu3Pd and Au3Zn compounds. In the Al3Ti, 1D-LPS of the types <21j> and <2j1> have energies which are very near those of D023 and D022. In Cu3Pd, <3>, <4>, and <43> 1D-LPS have similar energies of formation and are the more stable 1D-LPS's at T=0K. In Au3Zn, D023 structure is the ground state at T=0K, however <32j> 1D-LPS's have energies which are very near. The energetic results are discussed in the framework of the axial-next-nearest-neighbor using (ANNNI) model. In each system the antiphase boundary energy is calculated.

10:15 AM Break

10:30 AM

Incorporating Vibrational Entropies in First-Principles Calculations of Phase Equilibria: *Vidvuds Ozolins*[1]; [1]Sandia National Laboratories, Thin Film & Interface Sci., PO Box 969, MS 9161, Livermore, CA 94551-0969 USA

Recently, it has been demonstrated that the accuracy of first-principles calculated phase diagrams can be dramatically improved by including vibrational contributions to the free energies of alloy phases. For instance, vibrational entropy increases the solid solubility of Sc in FCC Al matrix by a factor of 27, bringing the calculated and experimentally measured solvus boundaries in excellent agreement [see V. Ozolins and M. Asta, Phys. Rev. Lett 86, 448 (2001)]. We find similar strikingly large effects in other Al-based alloys (such as Al-Au, Al-Cu, Al-Mg, Al-Ni, Al-Ti, and Al-Zr). These surprising results have added urgency to the development of new methods for incorporating vibrational entropies in first-principles calculations of alloy phase diagrams. We will discuss the prospects for accomplishing this goal in the framework of a generalized cluster expansion in terms of alloy configuration variables and ionic displacements. Using first-principles calculated vibrational spectra and interatomic force constants, we analyze in detail the configuration dependence of interatomic bond lengths and associated bond stiffness constants in the aforementioned Al-based systems. In particular, we stress the importance of including higher-order anharmonic terms in displacement variables. We also present a comparison with existing cluster expansion methods and discuss implications for treating elastic inhomogeneities and strain energies in coherent microstructures.

11:00 AM

First-Principles Thermodynamic Theory of Ordering in Multi-component Alloys: *Duane D. Johnson*[1]; [1]University of Illnois, Urbana-Champaign, Dept. of Matls. Sci. & Eng., 1302 W. Green St., Urbana, IL 61801 USA

A first-principles thermodynamic theory of atomic (and magnetic) short-range order for multicomponent alloys is presented. The alloy's ordering is based on the underlying electronic-structure of the high-temperature solid solution phase (using coherent-potential approximation and multiple-scattering theory) so its electronic origin can be determined. In this linear-response method, multicomponent alloys cost no additional computational time over binaries and all possible orderings on a given lattice can be determined in one calculation, similar to phonon modes. Examples in binary and ternary alloys (e.g., fcc Ni3V, bcc Ti-Al-Nb and Cu2AuZn) will be given, in some cases with comparison to results of structural inversion method or direct calculations of energetics in partially ordered alloys.

11:30 AM

Automating First-Principles Phase Diagram Calculations: *Axel van de Walle*[1]; Gerd Ceder[2]; Mark Asta[1]; [1]Northwestern University, Dept. of Matls. Sci. & Eng., 2225 N. Campus Dr., Evanston, IL 60208 USA; [2]Massachusetts Institute of Technology, Dept. of Matls. Sci. & Eng., Rm. 13-5056, 77 Massachusetts Ave., Cambridge, MA 02139 USA

The determination of phase diagrams from first principles is among the most important steps required to build a "virtual laboratory" where materials could be designed from first-principles, without relying on experimental input. The thermodynamic stability (or metastability) of a new material is important to assess, before spending a considerable amount of time to devise a way to synthesize it. Although the formalism that allows the calculation of solid state phase diagrams from first principles is well established, its practical implementation remains a tedious process. To solve this problem, we have created a software package which automates the process of performing such calculations. This talk will first describe the overall organization of the package, emphasizing its modular design. The algorithm underlying the automated construction of the so-called cluster expansion will be briefly discussed. Special attention will then be given to the methods enabling the automatic computation of various thermodynamic quantities through Monte Carlo simulations. Finally, various detailed examples of application will illustrate the package's ease of use.

Creep Deformation: Fundamentals and Applications: Aluminum Alloys

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

Program Organizers: Rajiv S. Mishra, University of Missouri, Metallurgical Engineering, Rolla, MO 65409-0340 USA; James C. Earthman, University of California, Department of Chemical and Materials Science, Irvine, CA 92697-2575 USA; Sai V. Raj, NASA Glenn Research Center at Lewis Fields, Cleveland, OH 44135 USA

Wednesday AM	Room: 214
February 20, 2002	Location: Washington State Conv. & Trade Center

Session Chair: W. Blum, University of Erlangen-Nuernberg, Inst. f. Werkstoffwissenschaften LS1, Martensstr. 5, 91058 Erlangen Germany

8:30 AM Keynote

Creep and Creep Fracture of Aluminium Alloys for Supersonic Civil Aircraft: *B. Wilshire*[1]; H. Burt[1]; [1]University of Wales Swansea, Dept. of Matls. Eng., Singleton Park, Swansea SA2 8PP UK

The low specific gravity of conventional aluminium alloys (~2.8 Mg m^{-3}) has ensured their widespread selection for airframe applications, but the low melting point of aluminium (Tm ≅ 933K) means that their creep properties must be considered when exposure temperatures approach $0.4T_m$. Such temperatures can be reached not only with parts deliberately heated for de-icing and cabin heating or components near the engines but also for critical areas of supersonic aircraft subject to kinetic heating. Thus, with Concorde, the critical temperatures must not exceed about 400K, limiting the speed to Mach 2.2. Major research programmes have therefore been launched, seeking to identify materials which may prove superior to the current Concorde alloy, Hiduminium RR58, an alloy containing approximately 2.5%Cu-1.5% Mg-0.2% Si-1.0% Fe-1.0% Ni (wt%). In particular, at Swansea, creep and creep fracture studies have been carried out for three conventional alloys having the following nominal compositions: 2124-T851, ie Al-4.4% Cu-1.5% Mg-0.6% Mn, 2419-T851, ie Al-6.3% Cu-0.15% Zn-0.3% Mn, and 7010-T7351, ie Al-6% Zn-2.4% Mg-1.7% Cu-0.3% Zr. In short-term tests at 423K, 2124-T851 displays the greatest resistance to creep and creep fracture. However, comparable properties are exhibited by 8090-T8771 (i.e. Al-1.3% Cu-1% Mg-0.1% Zr-2.5% Li), an interesting result because this aluminium-lithium alloy has a specific gravity (2.53 Mg m^{-3}) which would offer airframe weight savings approaching those expected with fibre-reinforced polymer composites. Yet, while short-term data provides information for performance ranking, the service lives of future high-speed civil transport will be 100,000 hours or more. For this reason, long-term stress-rupture property comparisons have also been undertaken to assess the creep and creep rupture strengths of 2124-T851 and 2419-T851 in relation to the property values reported for Hiduminium RR58 and the equivalent alloy, 2618.

9:00 AM
Creepal Thematic Network: Achievements and Future Challenges: *J. C. Ehrström*[1]; Y. Girard[2]; [1]Pechiney CRV, BP 27, 38341 Voreppe, Cedex France; [2]EADS CCR, 12 rue Pasteur, BP76, 92152 Suresnes, Cedex France

The CREEPAL EC funded thematic network worked between 1999 and 2001 to assess the present knowledge on the behaviour of aluminium alloys in creep conditions. The applications of aluminium alloys at high temperature include supersonic aircraft, car engines, turbines, conductors. Wrought 2000 and 6000 alloys and casting alloys (Al-Si-Mg-(Cu)) are particularly suited for these applications. The practical aspects of characterising small deformation creep (0.1% in 1000 h) were addressed via a round robin between 7 laboratories. The test conditions were compared thoroughly and the results statistically analysed. Good practices are defined which ensure consistency of the results between labs. The intrinsic scatter of the repeated tests in the same labs and conditions appears to be high compared with a CONCORDE type specification. Beside monotonic constant load creep, the practical components are submitted to complex loading sequences which result in damages due to fatigue and creep as well as thermal fatigue. These aspects are particularly important in car engines for instance. The damage tolerance of future supersonic aircraft structures i.e. resistance to sustained load cracking, fatigue cracking and residual strength, must be addressed taking into account the complex loading. New sheet material for high temperature application (AA2650) have been developed in the last decade. However, a better understanding of the micro-structural features controlling the behaviour of aluminium alloys at high temperature must be achieved in order to improve the performance of materials in real components. Several experts contributed to a state of the art on this subject. Strain induced ageing, glide types, effect of the different type of precipitates and substructure were addressed. Finally, the long term prediction, i.e. the extrapolation of data obtained with tests of limited duration to the real life time of the structures is a major issue in high temperature application. Empirical approaches as well as physically based approached were evaluated. Among metals, aluminium alloys are not often used for high temperature applications. They offer however unique compromises in the range 100°C-300°C thanks to their thermal conductivity, strength, forming and damage tolerance. The need to continue the investigations for a better performance of highly technological products appears clearly. The approach must include the knowledge gained in the development of other metals.

9:20 AM
Tertiary Creep in a Precipitation Hardened Al-Alloy Due to Dynamic Transformation of Precipitates: *Philip Eisenlohr*[1]; Wolfgang Blum[1]; Massimo De Sanctis[2]; [1]University of Erlangen-Nuernberg, Inst. f. Werkstoffwissenschaften LS1, Martensstr. 5, Erlangen 91058 Germany; [2]University of Pisa, Dipartimento di Ingegneria Chimica, Chimica Industriale e Scienza dei Materiali, Via Diotisalvi 2, Pisa 56126 Italy

The present work was performed within the European CREEPAL thematic network in order to check the microstructural origin of tertiary creep in Al-alloys hardened by metastable, (semi-) coherent precipitates. An AlSiCuZnMg-alloy was subjected to creep at 150°C. A minimum of creep rate followed by tertiary (accelerating) creep was found in compression. Transmission electron microscopy confirmed the aging of the precipitate structure by coarsening and transformation to the stable precipitate phase. The aging causes loss of precipitation hardening which is responsible for the onset of tertiary creep in compression. The localization of strain during creep indicates that the dislocation activity during creep enhances the aging process.

9:40 AM
Primary Creep in Precipitation Hardened Aluminium Alloy RR58: J. T. Evans[2]; *J. S. Robinson*[1]; R. L. Cudd[3]; [1]University of Limerick, Dept. of Matls. Sci. & Tech., Ireland; [2]University of Newcastle upon Tyne, Dept. of Mechl., Matls. & Mfg. Eng.; [3]Formerly of HDA Forgings, Ltd., Redditch, Worcestershire

The CEC funded Thematic Network CREEPAL (BRRT-CT98-5101) was established in 1998 to collect and disseminate information on the long-term creep and thermal mechanical cycling behaviour of aluminium alloys. Through CREEPAL, the opportunity has arisen to analyse a large experimental data set for the alloy Hiduminium RR58 (2618A) provided by HDA Forgings Ltd. (UK). Analysis of creep curves resulting from tests performed at 100°C indicates a substantial primary creep region. A continuum model of inhomogeneous deformation is presented in which the alloy is considered to consist of a matrix containing domains with a lower creep resistance than the matrix. It is shown that the model could account for the primary creep exhibited by the precipitation-hardened aluminium alloy RR58 at 100°C. A feature of the deformation in the model is the build up of internal stress, which will drive reverse deformation when the material is unloaded.

10:00 AM Invited
Precipitation Strengthening of Heat-Treatable Al(Sc) Alloys at Elevated Temperatures: *Emmanuelle A. Marquis*[1]; David N. Seidman[1]; David C. Dunand[1]; [1]Northwestern University, Dept. of Matls. Sci. & Eng., MLSB 2036, 2225 N. Campus Dr., Evanston, IL 60208-3108 USA

To understand the precipitation-strengthening parameters controlling optimal yield strength and creep resistance at elevated temperature, we studied the effects of precipitate size and volume fraction upon the yield and creep strengths of dilute Al(Sc) alloys in the temperature range of 225 to 300°C. Coherent, spheroidal Al_3Sc precipitates in alloys with 0.1, 0.2 and 0.3 wt.% Sc (corresponding to precipitate volume fractions in the range of 0.23 to 0.68%) were grown to sizes in the range 1.4 to 10 nm through different heat-treatments. Creep threshold stresses were found to be about ten times lower than the yield stresses at 300°C, indicative of a climb-controlled bypass mechanism, which is modeled according to existing theory. Transmission electron microscopy observations of deformed samples illustrate the interactions between dislocations and precipitates.

10:20 AM Break

10:30 AM Invited
Modelling Creep Ductilities and Lifetimes in a Commercial Aluminium Alloy: *Brian Dyson*[1]; [1]Imperial College of Science Technology & Medicine, Dept. of Matls. Prince Consort Rd., London SW7 2BP England

In a recent paper (1), Wilshire and Burt comprehensively analysed the tensile creep and fracture behaviour of the commercial aluminium alloy 2124-T851. They also showed that the accuracy of predicting service lifetimes using the θ methodology was seriously compromised because of uncertainties over expected creep ductilities, ε_f, at service stress levels. This led them to conclude that "a predictive knowledge of the factors determining ε_f remains a key requirement for low-ductility materials". The present paper attempts to provide a quantitative explanation. There seems little doubt that the creep fracture path in this (and similar aluminium alloys) is intergranular and that the detailed mechanism is dominated by the kinetics of intergranular cavitation. The paper revisits earlier work on creep-constrained cavitation and extends a previous analysis to obtain a numerical method which allows prediction of isothermal creep ductility during the stress range when the constrain t condition is gradually being relaxed. Applying the analysis to the 2124-T851 alloy reveals a simplifying if surprising feature: the rapidly increasing ductility with stress at each of the three temperatures analysed by Wilshire and Burt (1) and giving rise to their extrapolative problems–is quantitatively consistent with the transition from constrained to unconstrained growth of an array of cavities having a lower-bound ductility of 1.5%, independent of temperature. It thus provides an answer to the problem posed by Wilshire and Burt. Furthermore, it is shown that when this extended ductility model is incorporated within a hyperbolic sine law kinetic model of creep, it predicts the lifetimes and minimum creep rate data reported by Wilshire and Burt and also confirms their view that the very high and variable "n" values reported in these alloys (from 8-40) is not a consequence of any change of creep mechanism. 1. B. Wilshire and H. Burt, (2001) in Creep & Fracture of Engineering Materials & Structures, edited by J D Parker, The Institute of Materials, London, 261-268.

10:55 AM
Influence of Sub-Structure and Sub-Structure Development on the Creep of Aluminum Alloys: *Donald R. Lesuer*[1]; Rustam Kaibyshev[2]; [1]Lawrence Livermore National Laboratory, L-342, Livermore, CA 94551 USA; [2]Institute for Metals Superplasticity Problems, 39 Khalturina St., Ufa Russia

It is well know that subgrains have a pronounced effect on the elevated temperature plastic flow behavior of coarse-grain, polycrystalline aluminum and aluminum alloys. In general, if a sub-structure develops, then the strain rate at a given applied stress varies with subgrain size (l) as l3. However, the development and stability of substructure is a function of microstructure (especially dispersoid content), temperature and stress (subgrain size varies inversely with stress). In this paper, the creep behavior of a 2219 aluminum alloy is examined relative to the development and stability of its substructure. The alloy was processed to develop a microstructure containing nano-scale Al3Cr and Al3Zr dispersoids and the creep response was evaluated in the temperature range from 250-500°C. In the high stress/low temperature region, the creep data shows a stress exponent of 7 and the formation of weak cell boundaries, whereas in the low stress/high temperature region, a stress exponent of 5 and subgrains are obse rved. The creep behavior and substructure development in this alloy will be compared to the behavior of pure aluminum and other dispersion-containing aluminum alloys. Work performed under the auspices of the US Department of Energy by the Lawrence Livermore National Laboratory under contract No. W-7405-ENG-48.

11:15 AM
Deformation Behavior of a Modified 5083 Aluminum Alloy: *Rustam Kaibyshev*[1]; Oleg Sitdikov[1]; Fanil Musin[1]; [1]Institute for Metals Superplasticity Problems RAS, Khalturina 39, Ufa 450001 Russia

The deformation behavior of a 0.2% Zr and 1.6% Mn modified 5083 aluminum alloy was studied in the temperature range 250-570°C over five orders of magnitude of strain rate. It was shown that the modified 5083 Al exhibits a threshold behavior. Analysis in terms of threshold stress showed that there are three different classes of deformation behavior in the power-law creep regime which correspond with three different temperature dependencies of normalized threshold stress, distinguished by value of the energy term, Qo. At the lower values of normalized strain rates, kT/(D1Eb)<10-13, the true stress exponent, n, is close to 3 and the true activation energy, Qc, is about 130±5 kJ/mol. At normalized strain rates, kT/(D1Eb), ranging from 10-13 to 10-8 the n value is 4 and the true activation energy, Qc, is equal to 140±8 kJ/mol. At higher values of kT/(DlEb) (>10-8), the true stress exponent is 6 and the true activation energy is about 120±8 kJ/mol. The values of Qo were found to be about 31, 17 and 94 kJ/mol in the temperature intervals 250-350°C, 350-525°C and 525-570°C, respectively. The disappearance of threshold stress takes place at temperatures higher than 5500°C at strain rates lower than 10-5 s-1. Deformation mechanisms operating in the 5083 Al and their relations with threshold stress are discussed.

11:35 AM
Deformation Behavior of an Al-Li Alloy: *Rustam Kaibyshev*[1]; *Fanil Musin*[1]; *Donald Lesuer*[2]; [1]Institute for Metals Superplasticity Problems of RAS, Khalturina 39, Ufa 450001 Russia; [2]Lawrence Livermore National Laboratory, L-342, PO Box 808, Livermore, CA 94551 USA

The deformation behavior of a 1463 aluminum alloy (Al-2.1%Li-3%Cu) strengthened by coherent Al3Sc dispersoids was studied in the temperature range 250-480°C. It was found that the 1463 alloy exhibits threshold creep behavior. Analysis in terms of threshold stress revealed that at normalized strain rates, kT/(D1Eb) <10-9, the n value is 3. At higher normalized strain rates the true stress exponent is 5. The true activation energy, Qc, tends to grow from 90 kJ/mol at T=250°C to 142 kJ/mol at T=450°C with increasing temperature. Two different temperature dependencies distinguished by value of an energy term, Qo, were found. In the temperature range 250-450°C Qo is equal to 55 kJ/mol, and in the temperature intervals 450-480°C, Qo is about 22 kJ/mol. An effect of Al3Sc dispersoids on deformation mechanisms is discussed.

Deformation and Stresses in Small Volumes: Length and Size Scaling in Deformation

Sponsored by: ASM International: Materials Science Critical Technology Sector, Structural Materials Division, Jt. Mechanical Behavior of Materials
Program Organizers: David F. Bahr, Washington State University, Department of Mechanical & Materials Engineering, Pullman, WA 99164-2920 USA; Eric Kvam, Purdue University, School of Materials Engineering, West Lafayette, IN 47907-1289 USA; Scott X. Mao, University of Pittsburgh, Department of Mechanical Engineering, Pittsburgh, PA 15261 USA; Neville R. Moody, Sandia National Laboratories, Livermore, CA 94551-0969 USA

Wednesday AM   Room: 303
February 20, 2002   Location: Washington State Conv. & Trade Center

Session Chair: Neville R. Moody, Sandia National Laboratories, PO Box 969 MS 9404, Livermore, CA 94551-0969 USA

8:30 AM Invited
A Volume to Surface Area Concept for Thin Film Fracture: *William W. Gerberich*[1]; John Jungk[1]; Alex Volinsky[2]; [1]University of Minnesota, Cheml. Eng. & Matls. Sci., 545 S.E. Washington Ave., Minneapolis, MN 55455 USA; [2]Motorola, Inc., Mesa, AZ USA

Previous indentation studies at extremely small depths less than 100 nm have verified that the surface energy provides a pivotal role in the Indentation Size Effect (ISE). Based on the ratio of volume work to surface work it has been shown that the surface work is substantial for such indentations. This has led to a length scale defined as V/S. With this further defined for indentation into thin films, a connectivity between elastic-plastic fracture mechanics and this length scale provides a crack resistance criterion. A simplifying assumption is that the indentation contact radius is commensurate with an initial crack size nucleating at the film/substrate interface, as confirmed by focused ion beam sections. An R-curve analysis is then derived for incremental crack growth. It is proposed that the resistance, GR, is not only proportional to the thickness and yield strength squared as in nearly all analyses, but that the GR value also scales with the one-half power of the incremental crack growth. Application to the delamination of Cu-thin films from silicon substrates is demonstrated.

9:00 AM
Indentation Size Effect-Limits of Conventional Deformation Behaviour: *Andrew J. Bushby*[1]; Ian Spary[1]; Nigel M. Jennett[2]; [1]Queen Mary, University of London, Dept. of Matls., Mile End Rd., London E1 4NS UK; [2]National Physical Laboratory, Matls. Ctr., Teddington UK

The indentation size effect, in which the hardness increases as the size of the indentation contact reduces, is well known. In those experiments indentation stress-strain curves were generated using spherical indenters with radii ranging from a few micrometres to several hundred mircometres and these were compared to data from conventional compression tests. Indenters of radius greater than 100 micrometres produced a single indentation stress-strain curve independent of indenter radius with a power law hardening coefficient equivalent to that in the compression tests. However, for smaller indenters the indentation stress-strain curves appeared at progressively higher pressures for smaller radius indenters. In this paper we model those experiments using finite element analysis methods. By inputting the compression stress-strain data to the model indentation stress-strain curves for the macro size indenters are reproduced. However, the model shows no length scale dependence for any size of indenter. We show that by offsetting the compression stress-strain curve in the strain axis and inputting this data to the model, the indentation behaviour of the smaller radius indenters can be modelled. This suggests that the indentation size effect is a result of an increase in the initial yield behaviour of the material and so does not conform to conventional deformation behaviour. Relationships between the strain offset, indenter radius and the indentation response are presented.

9:20 AM
The Indentation Size Effect and Hardening Mechanisms in Salt Crystals: *J. Greg Swadener*[1]; [1]Los Alamos National Laboratory, MST-8, MS-G755, Los Alamos, NM 87545 USA

For NaCl and LiF single crystals, indentation with a Berkovich indenter exhibits increased hardness for decreasing depth of penetration, which is know as the indentation size effect. The size effect in these crystals is similar to the effect observed in metals and can be accurately described by a dislocation mechanism model. In contrast to a Berkovich indenter, a spherical indenter does not give a size effect with depth, but can be used instead to determine the effect of work hardening. A combination of spherical and pyramidal indenters was used to separately determine the work-hardening behavior and a true material length scale. The increase in hardness due to work hardening and length scale effects was in agreement with a recently developed model based on geometrically necessary dislocations. In addition, specimens that had been hardened by radiation exposure were found to exhibit the same length scale effects as unexposed specimens. The radiation hardening produced a simple incremental increase in hardness, which was similar to the effect of work hardening.

9:40 AM
Localized Slip around Nanoindentations: Slip Steps and Pile Up: *Kevin A. Nibur*[1]; David F. Bahr[1]; [1]Washington State University, Mechl. & Matls. Eng., PO Box 642920, Pullman, WA 99164-2920 USA

Localized slip behavior has been examined in a BCC titanium alloy as a function of crystal orientation and hydrogen concentration. Previous models have suggested hydrogen may alter the cross slip behavior of dislocations. This theory has been investigated using a combination of nanoindentation, atomic force microscopy (AFM) and orientation imaging microscopy (OIM). Nanoindentation allowed dislocation motion to be studied without being influenced by macroscopic features such as grain boundaries and precipitates. Slip steps and spacings were measured using AFM and further quantified using OIM to determine the specific slip system of each band and the number of slip planes between steps, ranging between 100 and 300 slip planes per step depending on crystal orientation and hydrogen concentration. The frequency and magnitude of cross slipping was then linked to hydrogen concentration. The versatility of OIM allows these tests to be performed on common engineering materials without being limited to single crystals. Ultimately, the comparison between macroscopic out of plane deformation via pile up and microscopic deformation in terms of slip steps will aid in developing local plasticity models from which macroscopic flow behavior can be extracted from nanoindentation.

10:00 AM Break

10:30 AM
The Effects of Microstructural Length-Scales on the Strength of Metallic Multilayered Thin Films: *Amit Misra*[1]; John P. Hirth[1]; Richard G. Hoagland[1]; Harriet Kung[1]; [1]Los Alamos National Laboratory, Matls. Sci. & Tech. Div., MS G755, Los Alamos, NM 87545 USA

The strengths of metallic multilayers, composed of alternating layers of soft metals, approach theoretical limits when the bilayer periods are on the order of a few nanometers. Nanoindentation experiments have been used to elucidate the effects of microstructural length scales on the strength of sputter deposited metallic multilayers such as Cu-Nb. The length scales considered are: (i) the bilayer period, in the range of 2 nanometers to a few micrometers (for equal Cu and Nb layer thicknesses), (ii) the in-plane grain size, coarsened by annealing for a constant bilayer period, and (iii) the Cu to Nb layer thickness ratio at a constant bilayer period. The dependence of strength on the microstructural length scales is modeled using dislocation theory. At the micrometer to the sub-micrometer length scales, the dislocation pile-up based Hall-Petch model is applicable. At lower length scales, the strength of multilayers is interpreted in terms of the motion of single dislocations as Orowan-type loops that initiate plastic deformation in the softer phase, and then transmit across the Cu/Nb interface overcoming the resistance from the interface dislocation arrays. It is shown that the strength enhancement at nanometer length scales is primarily due to the stress needed for dislocation transmission across the Cu/Nb interfaces. This research is funded by DOE-OBES.

10:50 AM
Hardness Anisotropy and Surface Deformation around Vickers Indents in Single Crystals: Reina Martinez[1]; Mehdi Hakik[1]; *Pedro D. Peralta*[1]; [1]Arizona State University, Dept. of Mechl. Eng., Main Campus, PO Box 876106, Tempe, AZ 85287-6106 USA

Micro- and nanoindentation of polycrystalline materials often results in indents completely contained within a single grain, where the anisotropy related to single crystal deformation can have a strong effect on the material behavior. In this work, single crystals of two semi-brittle materials (pure $MoSi_2$ and Al-doped $MoSi_2$) and a ductile metal (copper) were indented to sub-micron depths on the (001) plane using a Vickers indenter, with the diagonals of the pyramid aligned along either <110> or <100> directions. The surface deformation around these indents was characterized using Atomic Force Microscopy. The results indicate that sink-in and pile-up behavior depend strongly on the in-plane crystallographic orientation of the diagonals of the indent, even for the soft copper single crystal. These results are discussed in terms of the anisotropy of hardening and deformation expected in the single crystals studied and the differences and similarities with respect to isotropic behavior.

11:10 AM
Study on Lamellar PST-TiAl by Nanoindentations and AFM: *Minhua Zhao*[1]; *Scott Mao*[1]; Huiping Xu[2]; J.M.K. Wiezorek[2]; [1]University of Pittsburgh, Dept. of Mechl. Eng., 648 Benedum Hall, 3700 O'hara St., Pittsburgh, PA 15261 USA; [2]University of Pittsburgh, Dept. of Matls. Sci. & Eng., 3700 O'Hara St., Pittsburgh, PA 15261 USA

PST(Polysynthetically twinned) Titanium Aluminide alloys have been receiving a lot of attention in high temperature applications due to their outstanding density specific properties. Since the lamellar size of PST-TiAl is in the micron or submicron scale, its mechanical properties cannot be accurately predicted by conventional plasticity theory. In this study, in-situ nano indentations were made by Hysitron nanoindentor, while topography of the sample was analyzed by Nanoscope III AFM. Size effect in PST-TiAl was illustrated by the theory of strain gradient plasticity.

Fatigue and Creep of Metal Matrix Composites: Fatigue of Metal Matrix Composites - I

Sponsored by: Structural Materials Division, Jt. Composite Materials Committee
Program Organizers: Nikhilesh Chawla, Arizona State University, Department of Chemical and Materials Engineering, Materials Science and Engineering Program, Tempe, AZ 85287-6006 USA; John J. Lewandowski, Case Western Reserve University, Department of Materials Science and Engineering, Cleveland, OH 44106 USA

Wednesday AM	Room: 206
February 20, 2002	Location: Washington State Conv. & Trade Center

Session Chairs: Nik Chawla, Arizona State University, Dept. of Cheml. & Matls. Eng., Tempe, AZ 85287 USA; John Lewandowski, Case Western Reserve University, Dept. of Matls. Sci. & Eng., Cleveland, OH 44106 USA

8:30 AM Keynote
Fatigue of Particle and Whisker-Reinforced Metal-Matrix Composites: *Javier LLorca*[1]; [1]Polytechnic University of Madrid, Dept. of Matls. Sci., E. T. S. de Ingenieros de Caminos, Madrid 28040 Spain

The reinforcement of metallic alloys with ceramic particles or whiskers has generated a new family of composite materials. They have matured during the last twenty years, and are currently used in structural components subjected to cyclic loads. This was partially possible thanks to a large research effort aimed at characterizing their behavior in fatigue. The results of this activity constitute a fairly coherent body which relates the micromechanisms of cyclic deformation to the overall fatigue performance. They are presented in this review, which is divided in seven sections. After the introduction, the microstructural changes induced by the dispersion of the ceramic reinforcements are described. This is followed by two sections devoted to an analysis of the micromechanisms of cyclic deformation from the microstructural and mechanical viewpoints. The next two sections are focused on the origins of crack nucleation and the kinetics of crack propagation upon cyclic loads. The overall fatigue performance of these composites is examined in the last part, which emphasizes their advantages and limitations as compared to the unreinforced counterparts. The effects of the processing, thermomechanical treatments, microstructural features, environmental factors and loading conditions are included in each section to provide a comprehensive picture of the fatigue performance of these composites.

9:10 AM Invited
Fatigue Crack Growth in Composites: *Kuntimaddi Sadananda*[1]; Ronald L. Holtz[1]; Asuri K. Vasudevan[2]; [1]Naval Research Laboratory, Matls. Sci. & Tech. Div., Code 6323, Washington, DC 20375-5000 USA; [2]Office of Naval Research, 800 N. Quincy St., Arlington, VA 22217 USA

Crack growth behavior in composites is analyzed using the Unified Approach to Fatigue Crack Growth developed by the authors. This approach is based on the fact that fatigue requires two load parameters

WEDNESDAY AM

for unambiguous description. Normally the stress intensity range, *K and load Ratio, R are used but the effects of load ratio are accounted for crack closure arising from pre-mature contact of the mating surfaces. Our analysis indicates that crack closure is either absent or its contribution is very small to have an effect. It is further shown that for fatigue crack growth, *K and Kmax are the two governing parameters providing two crack tip driving forces required for crack growth. Hence there are two thresholds that must be overcome for a crack to grow. Using this approach, the crack growth behavior in composites is analyzed examining the physical significance of these two thresholds in the composites.

9:40 AM
Mechanical Behavior of Al2O3 Fiber-Pure Aluminum Matrix Composites: *R. Prakash Kolli*[1]; Chris Hoppel[2]; Jonathan Montgomery[2]; Robert Dooley[2]; [1]United States Military Academy, Dept. of Civil & Mechl. Eng., West Point, NY 10996 USA; [2]US Army Research Laboratory, Aberdeen Proving Ground, MD 21005-5069 USA

The US Army is considering metal matrix composite (MMC) materials for ordnance applications such as lightweight projectiles and gun systems. Nextel 610 alumina fiber-reinforced pure aluminum, made by 3M Company, is a relatively low cost candidate material with a high specific strength. Tensile specimans with three different fiber orientations, 0°, 0°/90°, and +45° were tested in monotonic tensile loading and in tension-tension (R=0.1) fatigue. The stress-strain response and low cycle fatigue life were determined. The following mechanical and material properties were evaluated: ultimate tensile strength, modulus of elasticity in the longitudinal direction, and strain to failure. Preliminary evaluation of shear modulus, and Poisson's ratio was also conducted. Optical metallography and electron fractography was performed to investigate microstructural failure modes.

10:00 AM
Fracture and Fatigue Studies on Be-Al "Composite-Like" Materials: *Joel Larose*[1]; John J. Lewandowski[1]; [1]Case Western Reserve University, Matls. Sci. & Eng., 10900 Euclid Ave., White 400, Cleveland, OH 44106 USA

Be-Al alloys are composed of two phases: a Be-rich phase, which has high modulus (e.g. 287 GPa) and is semi-brittle, and an Al-rich phase, which has relatively low modulus (e.g. 70 GPa) and is ductile. This presentation will focus on aspects of the fracture and fatigue crack growth behavior of Be-Al alloys processed via different means. The alloys contain approximately 70vol% Be and 30vol% Al and possess a "Cermet-like" structure. The damage tolerance is investigated by means of fracture toughness tests (K_Q) and fatigue crack growth (da/dN vs. ΔK). Notched and fatigue precracked specimens were used to determine fracture toughness at different temperatures. The effects of changes in stress ratio (i.e. R) and test temperature on the fatigue crack growth behavior were also determined. Fracture surfaces and fracture paths were examined by both optical and scanning electron microscopy in order to document any changes in observed behavior. Research supported by ONR N00014-99-1-0237 with supply of materials by Brush Wellman, Inc.

10:20 AM Break

10:30 AM Invited
Cyclic Plasticity and Fatigue in Metal Matrix Composites: A Modeling Perspective: *Yu-Lin Shen*[1]; [1]University of New Mexico, Dept. of Mechl. Eng., Mechl. Eng. Bldg., Albuquerque, NM 87131 USA

Continuum-based numerical modeling has been extensively used in studying the thermomechanical behavior of composite materials. By endowing the matrix and reinforcement materials with appropriate constitutive properties, the global composite response and local field quantities can be obtained in a straightforward manner. This presentation is devoted to applying this methodology to cyclic deformation in discontinuously reinforced metal matrix composites. The basic hardening laws used for modeling metal plasticity and their effects on cyclic response are addressed. The disturbance of plastic flow path in the metal matrix, due to the presence of hard reinforcement, is illustrated. Non-uniform matrix plasticity gives rise to early composite yielding and the Bauschinger effect, which provides a mechanistic rationale of the experimental findings. The effects of reinforcement geometry and pre-existing damage on the accumulation of cyclic plasticity, which ultimately leads to fatigue failure, will also be presented. Finally, we will discuss the interaction between intermetallic inclusion particles and reinforcement particles, and its influences on the fatigue crack initiation of the composite.

11:00 AM
Effect of Particle Orientation Anisotropy on the Fatigue Behavior of Metal Matrix Composites: *Vasudevan V. Ganesh*[1]; Nikhilesh Chawla[1]; [1]Arizona State University, Dept. of Cheml. & Matls. Eng., PO Box 876006, Tempe, AZ 85287-6006 USA

Preferred orientation of reinforcement particles is commonly observed in extruded particle reinforced metal matrix composites. Recent modeling work has shown that while the particles have a relatively small aspect ratio, the elastic modulus of the composite is affected by the direction of applied load with respect to the orientation of the particles. In this study, we have studied the effect of fatigue behavior of a 2080/SiC/10p-T6 composite oriented transverse and longitudinal to the extrusion axis. Stress controlled fatigue tests were carried out at a frequency of 40 Hz and an R-ratio of -1. Microstructural analysis of the fatigued specimens through transmission electron microscopy was conducted to obtain an understanding of the evolution of dislocation structures and interactions with precipitates in the Al matrix. Surface replication was also conducted to examine the role of particle orientation on fatigue crack growth in these materials. Research sponsored by the Office of Naval Research under contract# N00014-01-1-0694 (Program Manager: A.K. Vasudevan).

11:20 AM
Strain Evolution in an Aluminum-Alumina Metal Matrix Composite during Cyclic Loading and Fiber Failure: *Jay C. Hanan*[1]; Geoff A. Swift[1]; Ersan Üstündag[1]; Bjorn Clausen[1]; Mark M. Bourke[2]; [1]Caltech, Matls. Sci., 138-78, Pasadena, CA 91125 USA; [2]Los Alamos National Laboratory, Matls. Sci. & Tech. Div., PO Box 1663, MS H805, Los Alamos, NM 87545 USA

The evolution of matrix strains, particularly after fiber failure is of significant interest in metal-matrix composites. A model composite consisting of a single alumina fiber quenched in an aluminum alloy matrix was engineered to fail at the fiber in the center of the gage section. Neutron and synchrotron X-ray diffraction were employed to observe deformations within the composite while statically loaded and unloaded in tension over several cycles. The fiber failed upon loading leaving the matrix intact. Both fiber and matrix strains were monitored during this process at various length scales. The diffraction results were compared to micromechanics models.

Fundamentals of Advanced Materials for Energy Conversion: Hydrogen & Tritium Storage

Sponsored by: Extraction & Processing Division, Process Fundamentals Committee
Program Organizers: Renato G. Bautista, University of Nevada-Reno, Department of Chemical and Metal Engineering, Reno, NV 89557-0136 USA; Dhanesh Chandra, University of Nevada-Reno, Metallurgical & Materials Engineering, Reno, NV 89557 USA

Wednesday AM — Room: 613
February 20, 2002 — Location: Washington State Conv. & Trade Center

Session Chairs: Michèle Gupta, Université Paris-Sud, Institut Sciences des Matériaux, UMR8647 Bât. 415, Orsay 91405 France; Robert H. Hsu, Westinghouse Savannah River Company, Aiken, SC USA; Dhanesh Chandra, University of Nevada-Reno, Metlgcl. & Matls. Eng., Mackay Sch. of Mines, MS 388, Reno, NV 89557 USA

8:30 AM Plenary
Overview of Metal Hydride Technology for Applications in Transportation and Space: *Robert C. Bowman*[1]; [1]Jet Propulsion Laboratory, MS 79-24, 4800 Oak Grove Dr., Pasadena, CA 91109 USA

After a brief survey of the various classes of the metal alloys and compounds that are suitable for hydrogen storage and energy conversion applications, a comparison will be made of their relevant critical properties. Subjects to be covered include hydrogen absorption and desorption pressure, total and reversible hydrogen storage capacity, reaction rate kinetics, initial activation requirements, susceptibility to contamination, and durability during long term thermal or electrochemical cycling. Applications to be considered are hydrogen storage as fuel, electrodes in batteries, gas separation and purification, thermal switches, and sorption cryocoolers. Past and future uses of metal hydrides on space flights will be described.

9:10 AM Plenary
Applications of Metal Hydride Technology in Tritium Processing Systems: *Joseph R. Wermer*[1]; [1]Los Alamos National Laboratory, Tritium Sci. & Eng. Grp., MS C348, Los Alamos, NM 87544 USA

Metal hydride technology is in many ways ideally suited for tritium processing plants. Metal hydride-based tritium processing systems have greatly increased the efficiency and safety of tritium processing operations. While older facilities relied on tanks to store tritium gas and mechanical pumps to store and transfer tritium, newer facilities employ metal hydride technology to store and pump tritium. Hydrogen isotope separation systems have also been developed which take advantage of the large isotope effect of certain metal hydrides. The use of metal hydride technology has reduced the size and complexity of many systems, while increasing overall reliability. The use of metal hydrides in tritium processing is still expanding, and examples will be given of new applications. An overview of current uses of the technology, tritium aging characteristics of the materials, and future research areas will be presented.

9:40 AM Plenary
Modelling Multicomponent Alloys for Hydrogen Storage: *Reiner Kirchheim*[1]; [1]Universität Göttingen, Institut für Materialphysik, Hospitalstr. 3-7, Göttingen D-37073 Germany

Hydrogen storage alloys used today are multicomponent and structurally disordered containing large fractions of dislocations and grain boundaries. The current status of modelling pressure composition isotherms and H-diffusivity for these hydrogen-metal systems will be reviewed. Most of the models are based on a distribution of site energies for hydrogen which arises from variations of the chemical nature of the nearest neighbouring metal atoms as well as from a variation of the interstitial size occupied by hydrogen. Model predictions are compared with experimental findings. Recent results on the interaction between dislocations, grain boundaries and phase boundaries on the one hand and hydrogen on the other hand are presented for model systems. Corresponding experimental results are obtained by small angle neutron scattering and by tomographic atom probe analysis.

10:10 AM Break

10:20 AM Invited
Amorphization of $GdFe_2$ by Hydrogen Absorption: *Dhanesh Chandra*[1]; Ricardo B. Schwarz[2]; [1]University of Nevada-Reno, Metlgcl. & Matls. Eng., Mackay Sch. of Mines, MS 388, Reno, NV 89557-0136 USA; [2]Los Alamos National Laboratory, Struct./Prop. Relations Grp., MST Div., MS G755, Los Alamos, NM 87545 USA

We have studied the reaction of hydrogen with $GdFe_2$, a Laves phase alloy. At room temperature and for a pressure of 1.3 MPa, the alloy absorbs reversibly 1.6 atoms of hydrogen per metal atom, forming $GdFe_2H_{4.8}$. At this temperature, the slow kinetics makes it difficult to remove all the hydrogen from the alloy within reasonable time and, for pressures below 10^3 Pa, the desorption isotherm deviates from the absorption isotherm. At intermediate temperatures and pressures, the reaction leads to the formation of a single-phase amorphous $GdFe_2H_x$ phase. This reaction is quite unusual in that, depending on the temperature and pressure of the transformation, the crystal-to-amorphous transformation is accompanied by either a gain or a loss of hydrogen. At temperatures above 525 K, hydrogen absorption causes the disproportionation of the $GdFe_2$ crystal into a two-phase mixture of GdH_x (x » 2) and bcc-Fe.

10:40 AM Invited
Electronic Structure of Hydrogen Storage Intermetallic Compounds: *Michèle Gupta*[1]; [1]Université Paris-Sud, Inst. Scis. des Matériaux, UMR8647, Bât. 415, Orsay 91405 France

We review our recent work on the electronic structure of hydrogen storage intermetallic compounds of AB5, AB2 and AB type, where A and B are transition elements. Using the results of ab-initio band structure calculations, we discuss the features of the electronic properties relevant to storage applications such as the factors controlling the stability, the maximum hydrogen absorption capacity, the H site occupancy; we also analyze the modification of some fundamental properties of the matrix such as superconductivity and magnetism on hydrogen absorption. The following examples will be presented: i) Effect of mono and polysubstitutions of Ni in LaNi5 by 3d and s-p elements (Mn,Fe,Co,Cu,Al,Sn). ii) Role of chemical bonding on the stability and hydrogen site occupancy of AB hydrides (A=Zr, B=Co,Ni). iii) Hydrogen induced change of the superconductivity of the C-15 Laves phases AB2 (A=Zr, Hf, B=V) and modification of the magnetic properties of YB2 (B=Mn,Fe). We review our recent work on the electronic structure of hydrogen storage intermetallic compounds of AB5, AB2 and AB type, where A and B are transition elements. Using the results of ab-initio band structure calculations, we discuss the features of the electronic properties relevant to storage applications such as the factors controlling the stability, the maximum hydrogen absorption capacity, the H site occupancy; we also analyze the modification of some fundamental properties of the matrix such as superconductivity and magnetism on hydrogen absorption. The following examples will be presented: i) Effect of mono and polysubstitutions of Ni in LaNi5 by 3d and s-p elements (Mn,Fe,Co,Cu,Al,Sn). ii) Role of chemical bonding on the stability and hydrogen site occupancy of AB hydrides (A=Zr, B=Co,Ni). iii) Hydrogen induced change of the superconductivity of the C-15 Laves phases AB2 (A=Zr, Hf, B=V) and modification of the magnetic properties of YB2 (B=Mn,Fe). We review our recent work on the electronic structure of hydrogen storage intermetallic compounds of AB5, AB2 and AB type, where A and B are transition elements. Using the results of ab-initio band structure calculations, we discuss the features of the electronic properties relevant to storage applications such as the factors controlling the stability, the maximum hydrogen absorption capacity, the H site occupancy; we also analyze the modification of some fundamental properties of the matrix such as superconductivity and magnetism on hydrogen absorption. The following examples will be presented: i) Effect of mono and polysubstitutions of Ni in LaNi5 by 3d and s-p elements (Mn,Fe,Co,Cu,Al,Sn). ii) Role of chemical bonding on the stability and hydrogen site occupancy of AB hydrides (A=Zr, B=Co,Ni). iii) Hydrogen induced change of the superconductivity of the C-15 Laves phases AB2 (A=Zr, Hf, B=V) and modification of the magnetic properties of YB2 (B=Mn,Fe).

11:10 AM Invited
Palladium-Coated Kielselguhr for Simultaneous Separation and Storage of Hydrogen: *Robert H. Hsu*[1]; J. E. Klein[1]; [1]Westinghouse Savannah River Company, Aiken, SC USA

Palladium finely dispersed in a substrate of kielselguhr, Pd/k for short, has been successfully used for hydrogen storage, separation and pumping for a number of years at the Savannah River Site (SRS). Recently SRS has developed a new pd/k flow through bed (FTB) prototype for separating hydrogen from other gases and simultaneously storing the hydrogen on palladium. The FTB uses single-pass liquid nitrogen cooling during hydrogen absorption/separation/storage and electrical heating for desorption/unloading of hydrogen. More than ten (10) absorption-desorption or loading/unloading cycles using hydrogen have been conducted with the new FTB prototype. Test results show that all design performance objectives have been successfully achieved: recover >95% of hydrogen gas from feed gas, produce 99.9% hydrogen product gas and < 5% hydrogen in discharge gas. This presentation will discuss characteristics of the palladium-coated kielseguhr or diatomaceous earth, design and operation of the FTB, and results of performance tests such as separation efficiency, hydrogen storage capacity and system heat transfer characteristics.

11:40 AM Invited
Hydrogen Sorption of Mg Based Mixtures Elaborated by Reactive Mechanical Grinding: *J.-L. Bobet*[1]; B. Chevalier[1]; M. Y. Song[2]; B. Darriet[1]; [1]Institut de Chimie de la Matière Condensée de Bordeaux, ICMCB, CNRS [UPR 9048], Université Bordeaux 1, 87 Ave. du Dr A. Schweitzer, 33608 Pessac, Cedex France; [2]Chonbuk National University, Div. of Adv. Matls. Eng., 664-14 1ga Deogjindong Deogjingu Chonju 561-756, S. Korea

Due to their high hydrogen storage capacity, lightweight, low cost and abundance in the earth's crust, magnesium is one of the most promising candidates for hydrogen storage materials. However, the hydriding-dehydriding reaction takes place at high temperature (i.e. 287°C) and is relatively slow. One of the ways to kinetically improve magnesium based hydrogen storage materials is by the (i) addition of metals and/or intermetallics and or (ii) application of high energy ball milling. The aim of this study was to show the influence of mechanical alloying under hydrogen (Reactive Mechanical Grinding) on the chemical properties (crystallographic and phase composition) and on the hydrogen storage properties of different mixtures Mg + additive (= metal, intermetallics or oxides). The use of Reactive Mechanical Grinding (MG under H2) on magnesium powder improves the hydrogen sorption properties. The hydrogenation of Mg starts in situ during the milling process that allows suppressing the activation procedure generally requested for Mg. The addition of metals (Co, Ni), which acts as a catalyst for the reaction of dissociation of H2, also leads to an improvement of the hydrogen sorption properties (but a strong dependence upon the milling time is reported). The addition of intermetallics such as YNi and YNi2 also leads to an improvement of the hydrogen absorption kinetic but the mechanism is different. In this case, the additive acts as a hydrogen "pump" and then enables the diffusion of hydrogen in the Mg matrix. It is also shown that the addition of oxides such as Cr2O3 also improve the kinetic on the contrary the addition of Al2O3 (same structure) or CeO2 do not improve it. The hydriding is generally determined to be a two-step process: nucleation and diffusion. A direct relationship exists between the nucleation duration and the specific surface. Increasing the milling time up to 5 hours allows to increase the specific surface. The diffusion is controlled by the number of crystallites per particle. A critical milling time exists below which the diffusion process is improved and beyond which no more improvement is observed (the maximum internal stress in the powder is also reached at this critical time). We also try to explain why Cr2O3 addition lead to an improvement of the kinetic as CeO2 and Al2O3 does not improve it.

Fundamentals of Structural Intermetallics: Strengthening and Microstructure of TiAl

Sponsored by: ASM International: Materials Science Critical Technology Sector, Structural Materials Division, Jt. Mechanical Behavior of Materials
Program Organizers: Young-Won Kim, UES, Inc., Materials & Processing Division, Dayton, OH 45432 USA; Kwai S. Chan, Southwest Research Institute, Department of Materials Science, San Antonio, TX 78284 USA; Vijay K. Vasudevan, University of Cincinnati, Department of Materials Science and Engineering, Cincinnati, OH 45221-0012 USA

Wednesday AM — Room: 615-616
February 20, 2002 — Location: Washington State Conv. & Trade Center

Session Chairs: Young-Won Kim, UES, Inc., Matls. & Proc. Div., 4401 Dayton-Xenia Rd., Dayton, OH 45432 USA; Marc Thomas, ONERA-DMMP, 29 ave. de la Div. Leclerc, Chatillon, Cedex 92322 France

8:30 AM Invited
Elevated Temperature Tensile Properties of Gamma TiAl: Marcus Zupan[2]; *Kevin J. Hemker*[1]; [1]Johns Hopkins University, Dept. Mechl. Eng., Baltimore, MD 21218 USA; [2]Cambridge University, Micromech. Ctr., Trumpington St., Cambridge CB2 1PZ UK

Deformation in two-phase TiAl alloys occurs most readily in the gamma-TiAl phase, and measurements of the elevated tensile properties of gamma-TiAl are needed to provide a solid foundation for modeling the mechanical performance of these alloys. Microsample specimens of single crystalline gamma-Ti 55.5at%Al oriented near the [001], [010] and [-110] crystallographic axes have been tested in both tension and compression at temperatures ranging from 500° to 1000°C. Measurements of the of the Young's modulus, coefficient of thermal expansion, and flow strength have been made as a function of temperature, crystal orientation and sense of the applied load. The Young's modulus and coefficient of thermal expansion measurements were found to be comparable to literature values, obtained at lower temperatures, and can be used to expand the range over which these properties are known. Anomalous dependence of the flow strength, measurable violations of Schmid's law and significant tension/compression asymmetries have been recorded at all orientations. This unusual tensile behavior has been related to the dissociation and cross-slip locking of superdislocations, and the details of this locking mechanism will be used to characterize the tension/compression asymmetry and the elevated temperature deformation behavior of this alloy.

9:00 AM
High Temperature Deformation Behavior of Gamma TiAl Alloy-Microstructural Evolution and Mechanisms: J. H. Kim[1]; T. K. Ha[1]; Y. W. Chang[1]; *C. S. Lee*[1]; [1]Center for Advanced Aerospace Materials, Dept. of Matls. Sci. & Eng., Pohang Univ. of Sci. & Tech., San 31, Hyoja-dong, Pohang 790-784 Korea

Enhancement of ductility and hot workability is an important issue in the gamma-TiAl alloys. To achieve such a goal, it is necessary to clarify the governing deformation mechanisms with the variation of temperature and microstructure. Present investigation was carried out to enlighten the high temperature deformation mechanism in view of the inelastic deformation theory. A series of load-relaxation tests, tensile tests and compression tests were conducted on two-phase gamma TiAl alloy at 800C to 1020C. Results of load relaxation test (e = 0.04) showed that deformation was well described by sum of grain matrix deformation and dislocation climb process. When the alloy was deformed up to e = 0.8, grain refinement was observed to occur due to dynamic recrystallization process. Correspondingly, the flow curve changed its shape significantly resulting the broad concave portion in the intermediate strain rate region, which indicates the operation of GBS at this large strain level.

9:20 AM
Work Hardening Stability and its Implication on Component Strength: *Jonathan Paul*[1]; Fritz Appel[1]; [1]GKSS Research Centre, Inst. for Matls. Rsrch., Max-Planck-Strasse, Geb45, WFP, Geesthacht, D-21502 D-21502 Germany

This paper studies the origin and thermal stability of the defects that give rise to work hardening during room temperature deformation. The investigations involve mechanical testing, electron microscope observations of the defect structure, and recovery experiments. The investigations indicate that work hardening is derived from long-range elastic interactions between dislocations on parallel and oblique slip planes. Another source of work hardening arises from dislocation dipoles and debris defects, which were trailed and terminated at jogs in screw dislocations. Removal of these defects through annealing gives rise to a significant recovery of the work hardening. Thus, most of the room temperature work hardening is lost after just a few hours exposure to operating temperatures (700-750°C). A novel heat-treatment/processing procedure that has the potential to increase high temperature strength has also been investigated. The method involves introducing work hardening through deformation and then performing a heat-treatment to stabilize deformation induced defect structure.

9:40 AM Invited
Effect of Y-Addition on the Mechanical Properties and Oxidation Resistance of TiAl-Mn-Mo: *Sun-Keun Hwang*[1]; Ying Wu[1]; [1]Inha University, Sch. of Matls. Sci. & Eng., 253 Yonghyun-Dong, Nam-Gu, Incheon 402-751 Korea

TiAl-based alloys with the nominal chemical compositions of Ti-46.6Al-1.4Mn-2Mo-0.3C-xY (x=0.1, 0.33 and 0.6), were developed with Elemental Powder Metallurgy method. The alloys with yttrium addition had higher ultimate tensile strength, elongation and oxidation resistance than the Y-free alloy. Combined solid solution strengthening of Mn, Mo, C and Y, and the microstructural refining effect of C and Y were responsible for the increased strength at room temperature as well as at high temperature up to 800°C. Besides, Y2O3 and carbide precipitation also enhanced the strength. The room temperature ductility was improved by the microstructural refinement and by the reduction of interstitial oxygen in the a2 and g matrix. The improved ductility was evidenced by dislocations with ordinary perfect Burgers vectors in deformed g phase. The improvement of oxidation resistance by yttrium addition was attributed to the reduction of the concentration of oxygen vacancies in the TiO2 scale.

10:10 AM
Interstitial Elements in Ternary Ti-Al-Cr Alloys: Microstructural Effects: *Mélanie Lamirand*[1]; Jean-Louis Bonnentien[1]; Michel Cornet[1]; *Jean-Pierre Chevalier*[1]; [1]CECM-CNRS, 15, rue Georges Urbain, Vitry, Cedex 94407 France

Microstructural modifications in Ti-Al-Cr as a function of controlled additions of O, C and N will be presented. Previous work on binary Ti48Al has shown that these interstitial elements affect significantly the proportion of alpha 2 and gamma phases in fully lamellar alloys. The alpha 2 volume fraction increases with increasing interstitial content, yielding a smaller interlamellar spacing, which results in a higher yield stress. Primary creep rate also showed a marked reduction as a function of increasing O, C and N content. This approach has been applied to the ternary Ti48AlCr2 alloy, using both ultra high purity (60 wt ppm oxygen) and commercial purity Ti associated with clean processing. Variable amounts of O, C and N have been added in a controlled manner, and the microstructure has been analysed using a field emission gun scanning electron microscope, for given heat treatments and cooling rates. The aim of this work is to ascertain whether the effects previously observed can be transposed to such ternary alloys. The study will also be extended to the duplex (gamma plus lamellar) microstructure. This work also explains, at least partially, the substantial scatter in properties observed in industrial grade alloys, where both the initial interstitial content and pick up of at least O during heat treatment is not necessarily systematically assessed.

10:30 AM
Characterization of Solute Partitioning in a TiAl-Based Alloy by the Quenching during Directional Solidification Technique: *Matthias Charpentier*[1]; Marjolaine Grange[2]; Dominique Daloz[1]; Elisabeth Gautier[1]; Alain Hazotte[1]; Gérard Lesoult[1]; [1]ENSMN-LSG2M, Parc de

Saurupt, Nancy, Cedex 54042 France; [2]SNECMA Moteurs, DT/DMP, Site de Villaroche, Moissy-Cramayel 77550 France

One major hindrance to effective application of cast gamma TiAl-based intermetallic alloys in aircraft engines lies in the variability of their mechanical properties resulting from chemical thus microstructural heterogeneities. In the present work, the build-up of microsegregation in a cast Ti-48Al-2Cr-2Nb alloy is investigated through experiments of quenching during directional solidification (QDS). The first solidification steps as well as the alloying elements partitioning between the solid and the liquid phases are clarified. The results are discussed with regard to the range of chemical heterogeneity determined within Ti-48Al-2Cr-2Nb investment cast parts. Regarding subsequent solid phase transformations, the study also tends to explain the formation of minor phases stabilised by the ternary additions.

10:50 AM
Phase Transformations in Multicomponent Gamma Titanium Aluminides: Zhihong Zhang[1]; Dennis M. Dimiduk[2]; *Vijay K. Vasudevan*[1]; [1]University of Cincinnati, Dept. of Matls. Sci. & Eng., Cincinnati, OH 45221-0012 USA; [2]Air Force Research Laboratory, Matls. Direct., WPAFB, Dayton, OH 45433 USA

Phase transformations and microstructure evolution in Ti-(45-47)Al-2Cr-2Nb-(0-1)Mo-(0-0.2)B and Ti-45Al-2Mn-2Nb-0.3 wt.%B XD alloys have been studied by electrical resistivity measurements, x-ray diffraction, scanning electron microscopy with back-scattered electron imaging and analytical transmission electron microscopy. Phase boundaries and transformation temperatures during heating and cooling were determined. The transformations of the high-temperature beta, alpha or both phases during continuous cooling, as well as during step-quench+isothermal holding were studied, and the competition in temperature and time space between the various transformation modes, namely, lamellar, cellular, feathery and massive gamma were ascertained. The structure and chemistry of phases present in alloys with and without boron were determined, and these were useful for establishing isothermal phase diagrams displaying the change in phase equilibria with alloying and temperature. Continuous cooling transformation diagrams were also established and detailed microscopy was performed to unravel transformation mechanisms associated with the various non-lamellar transformation modes (especially the cellular and feathery modes) and the influence of chemistry. Finally, experiments aimed at elucidating the effects of boron on transformations and microstructural evolution were performed. Based on the results obtained, explanations for the effects of the alloying additions and thermal history on microstructure evolution, transformation modes, mechanisms, kinetics and phase equilibria are provided. Support for this research from NSF Grant# DMR-9731349, Dr. Bruce MacDonald, Program Monitor and AFOSR Grant# F49620-95-1-0116, Dr. Craig Hartley, Program Monitor, is deeply appreciated.

11:20 AM
Influence of Alloying Elements on the Kinetics of Massive Transformation in Gamma Titanium Aluminides: Uttara Prasad[1]; *Mahesh C. Chaturvedi*[1]; [1]University of Manitoba, Dept. of Mechl. & Indl. Eng., 356 Engineering Bldg., 15 Gillson St., Winnipeg, Manitoba R3T 5V6 Canada

The effect of alloying elements, Nb and Mn on massive transformation in Ti-45Al based alloys was studied by heat treatment of the alloy samples at 1350°C for 30 minutes followed by cooling to room temperature at the rate of ~700°C/sec and subsequent microstructural characterization. The amount of massively transformed gamma was observed to increase from zero for 0 percent Mn to ~70 percent for 2 percent Mn. Nb had minimal influence on the rate of transformation. This effect of Mn and Nb has been rationalized on the basis of the site occupancy of the alloying elements and their influence on the phase boundaries and grain size. TEM analysis has also been conducted to understand the mechanism of massive transformation in these alloys. Based on the results obtained, the effect of Mn and Nb on the kinetics of massive transformation will be discussed and CCT diagrams for different alloys will be proposed.

11:40 AM
Influence of Oxygen on Phase Transformations in a Ti-48 at. % Al Alloy: *Williams Lefebvre*[1]; Annick Loiseau[2]; Alain Menand[1]; [1]Groupe de Physique des Matériaux, UMR CNRS 6634, Faculté des Sciences, 1 rue Thomas Beckett, Mont Saint Aignan 76 821 France; [2]Laboratoire d'Etude des Microstructures, UMR CNRS-Onera, Onera, BP 72, 29 av. de la Division Leclerc, Chatillon 92322 France

Near equiatomic Ti-Al alloys, especially the Ti-48 at. % Al alloy, have been intensively investigated during the last decade. It is now well established that Ti-48 at. % Al alloys can exhibit various microstructures, depending on the cooling rate from high temperature (i.e. 1670 K). Many studies have contributed to get a better understanding of phase transformations involved in this alloy. However, the influence of interstitial impurities (e.g. C, N, O) on phase transformations has not been sufficiently investigated. This kind of study is often difficult to make, as most analytical techniques cannot quantitatively analyse light elements. In this study, alloys with a Ti- 48 at. % Al base composition and various oxygen contents have been investigated by APFIM (Atom Probe Field Ion Microscopy) and TEM (Transmission Electron Microscopy). Unlike other analytical techniques, AP can detect all elements including light atoms. Heat treatments have been applied to obtain either lamellar (slow cooling rate) or massive structures (high cooling rate). Beyond the well-known oxygen scavenging effect of the $\alpha 2$ phase, it will be demonstrated that oxygen has an essential influence during both lamellar and massive transformations.

General Topics in Waste Treatment and Minimization: Environmental Thermal Treatments and Processes

Sponsored by: Extraction & Processing Division, Process Mineralogy Committee, Waste Treatment & Minimization Committee
Program Organizers: Junji Shibata, Kansai University, Department of Chemical Engineering, Osaka 564-8680 Japan; Cheryl Dahlin, US Department of Energy, Albany Research Center, Albany, OR 97321-2152 USA; Jasper Kwong, US Department of Energy, Albany Research Center, Albany, OR 97321-2198 USA

Wednesday AM — Room: 604
February 20, 2002 — Location: Washington State Conv. & Trade Center

Session Chairs: Jasper Kwong, US Department of Energy, Albany Rsrch. Ctr., 1450 Queen Ave. S.W., Albany, OR 97321 USA; Cheryl L. Dahlin, US Department of Energy, Albany Rsrch. Ctr., 1450 Queen Ave. S.W., Albany, OR 97321 USA

8:30 AM
Effect of Slag Viscosity on the Separation of PGM's during Electric Scrap Melting: *Jeong-Whan Han*[1]; Jae-Hong Zee[1]; Sin-Suk Han[1]; *Jae-Chun Lee*[2]; [1]Inha University, Sch. of Matls. Sci. & Eng., 253 Yonghyun-dong Namku, Inchon 402-751 Korea; [2]KIGAM, Recycling Rsrch. Ctr., 30 Gajeong-dong Yuseong-ku, Daejeon 305-350 Korea

A recovery of PGMs from spent printed circuit board(PCB) scraps has been investigated by using pyrometallurgical process. For this purpose vertical electrical resistance furnace and high frequency induction furnace were used for clacination and melting the scraps, respectively. In order to enhance PGMs separation from the scrap, various slag system were attempted to be used in the process and copper was used for collector metal to collect PGMs from the scrap. Main variables used in the experiments were the slag properties such as composition and temperature of the slags. High temperature viscometer was used to measure the viscosity of slag systems. It was found that viscosity of slag greatly influences on the separation of PGMs from the melted scrap.

8:50 AM
The Environmental Benefits from Computer Modeling EAF Slag Chemistry: *Kyei-Sing Kwong*[1]; James P. Bennett[1]; [1]US Department of Education, Albany Rsrch. Ctr., 1450 Queen Ave. S.W., Albany, OR 97321 USA

The recycling of MgO-C refractories as a slag conditioner in EAF (electrical arc furnace) foaming slags has been evaluated by ALRC. The amount of MgO in the slags is critical for the foaming quality. Good foaming slags provide the benefits of high energy efficiency and low refractory consumption and require saturation with MgO. A computer model predicting the chemistry of MgO saturated foaming slags was designed to predict suitable amount of MgO additives from MgO-C spent refractories. This model can also help to reduce the amount of slags and to improve the economics of producing steel. The implementation of this recycling program is underway at steel plants and the experience of recycling spent refractories will be discussed.

9:10 AM
Zinc Recovery from Eaf Dust through Thermal Reduction: *D. Mishra*[1]; N. Kanari[1]; I. Gaballah[1]; B. Dupré[2]; [1]Laboratorie Environmental et Mineralurgie, Minl. Proc. & Environml. Team, Rue du Doyen Marcel Roubault, BP 40, 54501, Vandoeuvre, Cedex France; [2]Laboratorie de Chimie du Solid Mineral, UHP Nancy 1 UMR 7555, BP 239, 54506, Vandoeuvre, Cedex, France

Electric arc furnace dust (EAFD) generated during the recycling of steel-scrap is classified as a hazardous waste for landfilling and dumping. This is because it contains leachable heavy metals such as zinc, lead? Recovery of these metals could result in both resources conservation and resolving waste disposal problems. A study of the thermal reduction of a sample of EAFD was carried out in an inert gas atmosphere using coke as a reducing agent. Preferential volatilization of zinc and lead was achieved during the reduction process at about 800°C. More than 96% of both zinc and lead were removed from the dust and were recovered in the condensates. The treatment residue was essentially composed of iron oxides and almost free from heavy metals.

9:30 AM
Behavior of Ceria as an Actinide Surrogate in Electro-Slag Remelting and Refining Slags: *Uday B. Pal*[1]; Timothy Keenan[1]; Ajay Krishnan[1]; William C. Chernicoff[1]; Christopher J. MacDonald[1]; Edward Chiang[1]; James Van Den Avyle[2]; M. A. Molecke[2]; D. Melgaard[2]; [1]Boston University, Mfg. Eng., 15 St. Mary's St., Boston, MA 02446 USA; [2]Sandia National Laboratory, Liquid Metals Proc. Lab., Albuquerque, NM 87185 USA

Downsizing and decommissioning of nuclear facility operations is increasing the stockpile of various different grades of Radioactive Scrap Iron (RSI). It is desirable to be able to decontaminate the RSI to a very low level that can be recycled or used for fabrication of containers for RSI disposal. Electro-Slag Remelting and Refining (ESR) is often used for decontaminating radioactive contaminated sources of scrap iron such as stainless steel. Non-radioactive oxides of cerium are used to simulate the radioactive oxide contaminants of Uranium and Plutonium. The success of the ESR process is strongly dependent on having the right thermo-physical-and-chemical slag properties. We measured the following relevant slag properties: capacity to incorporate the radioactive contaminant (simulant), volatilization rate and volatile species, electrical conductivity, viscosity, surface tension, slag-metal partition coefficient, and ceria dissolution kinetics as a function of temperature. The impact of these properties on the ESR decontamination process will be discussed.

9:50 AM Break

10:10 AM
A Plasma Assisted Cyclone Reactor for Vitrification: *Patrick Rodger Taylor*[1]; [1]University of Tennessee, Matls. Sci. & Eng., 435 Dougherty Engineering Bldg., Col. of Eng., Knoxville, TN 97996-2200 USA

A non-transferred arc thermal plasma assisted cyclone reactor has been designed, built and operated to evaluate its use in vitrification of wastes. Simulated waste (liquid, slurry or fine particulate) is injected near the plasma flame, where nearly instantaneous dehydration and calcination reactions happen. A non-transferred arc plasma torch was attached tangentially to the cyclone and is utilized as both an enthalpy source and to provide the gas velocities required to generate the cyclonic gas flow patterns. The closed top cyclone flow sends the solid particulates to the wall, where they are captured by a thin film of molten glass that is injected as a powder at a position lower in the reactor. The molten glass is then collected in a crucible. The feasibility of simulant injection directly into the flame zone and its effect on electrode lifetimes has been studied. Several candidate refractory systems have been evaluated for their suitability for extended use under the demanding conditions present in the cyclone reactor.

10:30 AM
Properties of Iron Phosphate Waste Forms: *Patrick Rodger Taylor*[1]; Wanqing Huang[2]; [1]University of Tennessee, Matls. Sci. & Eng., 435 Dougherty Engineering Bldg., Col. of Eng., Knoxville, TN 97996-2200 USA; [2]University of Idaho, Moscow, ID 83844-3024 USA

Iron phosphate glasses are promising host matrices for vitrifying actinide rich nuclear waste materials because of their high solubility of actinide oxides, high chemical durability and relatively low melting temperature. Viscosity measurements were made on iron phosphate over the temperature range of 1000 to 1200C. Partitioning behavior was studied for Ce and Sr. The results show that the viscosity behavior is very sensitive to the composition and that both Ce and Sr have high solubilities in the glass under the conditions studied.

10:50 AM
Understanding of Hazardous Waste Incineration through CFD Simulation: *Yongxiang Yang*[1]; Markus A. Reuter[1]; Jack Voncken[1]; Joep Verwoerd[2]; [1]Delft University of Technology, Dept. of Appl. Earth Scis., Mijnbouwstraat 120, Delft 2628 RX The Netherlands; [2]AVR-Chemie, Prof. Gerbrandyweg 10, Rotterdam-Botlek 3197 KK The Netherlands

Rotary kiln incinerators are widely used in the incineration of various types of hazardous wastes. However, the complex transport processes within the incinerator are not well understood. Due to large variations in waste types and difficulties in feed characterization, the incineration process meets great challenges in a smooth operation, and expects uncertainties in the process chemistry and emission control. In order to get better understanding of the incineration process, process simulation was made on the kiln behavior by using Computational Fluid-dynamics (CFD) to characterize gas flow, temperature distribution and waste combustion in the incinerator. Temperature measurement was conducted in an operating incinerator to validate the CFD model. This paper addresses the environmental issues related to the hazardous incineration process, and reports the recent simulation results on gas flow and mixing, combustion heat transfer, and potentials to reduce emissions (CO and dioxins).

11:10 AM
Environmentally Sound Technology for Processing of Domestic Solid Waste and Other Toxic Waste in Sparged Molten Slag: *A. V. Grechko*[1]; V. F. Denisov[1]; [1]State Research Center of Russian Federation, State Rsrch. Inst. of Non-Ferrous Metals "Gintsvetmet", 13, Acad. Korolyov St., 129515 Moscow Russia

An environmentally clean and virtually waste-less technology for treatment of toxic chloride-containing waste materials has been developed and proven on a full scale by the Gintsvetmet Institute in cooperation with other Russian organizations. The proposed process resolves the acute and globally significant problem of dioxin formation. The purpose of the proposed technology is to ensure a destruction of the structural lattice that would guarantee irreversible transformation of the resultant substances to prevent formation of dioxins. The preconditions that are required to achieve this purpose are a temperature >1250C; an oxidant excess coefficient >1.05; a retention time of the products under these conditions (>2 s); and a thermal instantaneousness of the process involving a transition with no intermediate phase. These conditions were achieved with the experimental development of the Vanyukov furnace design commonly used for sparged smelting processes at non-ferrous metallurgical plants in Russia and Kazakhstan.

High Performance Metallic Materials for Cost Sensitive Applications: Intermetallics

Sponsored by: Structural Materials Division, Structural Materials Committee, Titanium Committee
Program Organizers: Edward Y. Chen, TiTech International, Inc., Pomona, CA 91768 USA; Rod Boyer, Boeing Commercial Airplane Group, Seattle, WA 98124-2207 USA; F. H. (Sam) Froes, University of Idaho, Institute of Materials and Advanced Processes, Moscow, ID 83844-3026 USA; Eric M. Taleff, University of Texas, Mechanical Engineering Department, Austin, TX 78712-1063 USA

Wednesday AM — Room: 213
February 20, 2002 — Location: Washington State Conv. & Trade Center

Session Chairs: Deliang Zhang, University of Waikato, Hamilton New Zealand; Sunil N. Patankar, University of Idaho, Moscow, ID 83844 USA

8:30 AM
Thermal Stability of Alumina Mold against Molten Ti-Al Alloys: *Myoung-Gyun Kim*[1]; Si-Young Sung[1]; Hee-Kook Kim[1]; *Young-Jig Kim*[1]; [1]Sungkyunkwan University, Sch. of Metlgcl. & Matl. Eng., 300, Chunchun-dong, Changan-gu, Suwon, Gyounggi-do 440-746 Korea

Investment casting of titanium aluminides has received a considerable attention in the cost-saving process because of their poor workability and ductility. Especially, the selection of mold material is essential for investment casting of titanium aluminides due to their high reactivity in the molten state. Alumina is regarded as a promising investment mold material in terms of formability, cost and thermal stability from the previous study. In order to investigate the thermal stability of alumina mold against molten Ti-Al alloys, the Ti-(10¡-55)at% Al alloy buttons were prepared by melting and casting in a plasma arc melting furnace under argon atmosphere. The selections were based on the Ti-Al binary phase diagram. The cast microstructures of interface between Ti alloy and alumina mold have been studied as a function of composition using optical microscope, electron probe X-ray microanalyzer and hardness measurement.

8:50 AM
Grain Size Control in Ti-48Al-2Cr-2Nb with Yttrium Additions: *Pankaj Trivedi*[1]; E. G. Baburaj[1]; S. N. Patankar[1]; F. H. (Sam) Froes[1]; A. Genc[2]; L. Ovecoglu[2]; [1]University of Idaho, Inst. for Matls. & Adv. Proc. (IMAP), Mines Bldg., Rm. 321, Moscow, ID 83844-3026 USA; [2]Istanbul Technical University, Istanbul, Turkey

Gas atomized powder of the Ti-48Al-2Cr-2Nb intermetallic with additions of 1.6 wt. % Y were mechanically alloyed (MA'd) and hot isostatically pressed (HIP'd) to produce fully dense nanocrystalline material. MA of the as blended powder for 16 hrs resulted in the formation of a disordered fcc phase. HIP'ing of the alloy powder produced a single-phase nanocrystalline TiAl intermetallic, containing a distribution of 5-10 nm sized Al2Y4O9 particles. The formation of oxide particles occurred by the chemical combination of Al and Y with oxygen, the latter element entering as a contamination during milling. Oxide particles increased the strength of the intermetallic compound and minimized grain growth even at 0.8Tm, where Tm is the melting point of the compound.

9:10 AM
Synthesis and Consolidation of Nanocrystalline Titanium Aluminides: E. G. Baburaj[1]; C. Draney[1]; R. Fielding[1]; F. H. (Sam) Froes[1]; S. Thevuthasan[2]; V. Shutthanandan[2]; [1]University of Idaho, Inst. for Matls. & Adv. Proc. (IMAP), Mines Bldg., Rm. 321, Moscow, ID 83844-3026 USA; [2]Pacific Northwest National Laboratory, Environmental Molecular Scis. Lab., Richland, WA 99352 USA

Nanocrystalline TiAl based intermetallics have been produced by mechanical alloying (MA'ing) followed by reaction during hot isostatic pressing (HIP'ing). In this process titanium hydride and aluminum powders are milled to an ultrafine size followed by HIP'ing to form the hydrided Ti-Al. The advantages of the process are the ease of alloy formation and auto-hydrogenation of the ultrafine powders to passivate the powders against oxidation during consolidation. Studies on dehydrogenation of consolidated samples using resonant Nuclear Reaction Analysis (NRA) revealed a concentration gradient of hydrogen in TiAl samples as a function of depth from the surface and complete removal of hydrogen from the TiAl lattice by vacuum annealing. The effect of hydrogen in TiAl as a temporary alloying element will be discussed in detail.

9:30 AM
Production of γ-TiAl Sheets with Improved Superplastic Properties by Pack Rolling: *M. R. Shagiev*[1]; G. A. Salishchev[1]; F. H. (Sam) Froes[2]; [1]Institute for Metals Superplasticity Problems, 39 Khalturin Str., Ufa-450001 Russia; [2]University of Idaho, Inst. for Matls. & Adv. Proc. (IMAP), Mines Bldg., Rm. 321, Moscow, ID 83844-3026 USA

The sheets of γ-TiAl based alloys with improved superplastic properties are of a great interest for aerospace applications. Such properties can be achieved through the grain refinement to micron and submicron level. Grain refinement may also lead to considerable decrease in the temperature intervals of brittle-to-ductile transition and, consequently, of pack rolling. Therefore, the smaller the grain size in rolling preform and the lower the rolling temperature, the higher superplastic properties in the sheet. Besides the microstructure improvement in γ sheets, decrease in rolling temperature will decrease their cost because of energy savings and use of the cheap can materials. The temperature intervals of pack rolling of several γ alloys were defined based on tensile properties at strain rates corresponding to rolling ones. Optimization of texture and rolling regimes were performed in order to eliminate anisotropy of superplastic properties in the sheet. Pack rolling temperature of Ti-50Al alloy with homogeneous microcrystalline structure was found to be 950°C while that of Ti-45Al-2Cr-2Nb-0.45B alloy was 1100°C. At 1000°C and strain rate of 10-3 s-1, both sheets exhibited elongations of about 200% and steady state flow stresses of 140 MPa.

9:50 AM Break

10:10 AM
Chemical Reaction Behaviour of Titanium Aluminides and α-Al2O3 with NaOH Aqueous Solution: *G. Adam*[1]; Deliang Zhang[1]; [1]University of Waikato, Dept. of Matl. & Proc. Eng., PB 3105, Hamilton, New Zealand

Titanium metal and titanium alloys are materials of high value, because of their high specific strength, high corrosion and oxidation resistance and good biological compatibility with human tissues. Although they are mainly used in aerospace and chemical processing industries, titanium metal and alloys are particularly attractive to the automotive industry. However, they have not been widely used in manufacturing automobiles, because of their high cost. Development of the ways in which the cost of producing titanium metal and alloys has a significant implication in the pursuit of making lighter and lighter vehicles. As part of a study which aims at developing techniques of extracting titanium alloys or titanium based intermetallic compounds, we investigated the reactions of Ti3Al, Al3Ti and Al2O3 fine particles with caustic solutions under different conditions. Reactions of alpha alumina (α-Al2O3) with caustic solutions have been previously studied, but there has not been much research work on the reactions between titanium aluminide powders and caustic solutions. This paper is to present and discuss the results of this investigation and the implications of the results in developing an alternative process of extracting titanium metal from titanium containing minerals.

10:30 AM
Processing and Properties of Titanium Aluminide-Ceramic Composite Materials: *Deliang L. Zhang*[1]; Z. H. Cai[1]; J. Liang[1]; G. Adam[1]; [1]University of Waikato, Dept. of Matls. & Proc. Eng., PB 3105, Hamilton New Zealand

Titanium aluminides (Al3Ti, TiAl and Ti3Al)-ceramic composite materials are important materials due to their high specific modulus, high specific strength, high creep resistance and good oxidation resistance. Depending on the matrix phase and the desired ceramic reinforcement features, This type of materials can be synthesized by either reacting TiO2 with Al or mechanical alloying Ti and Al elemental powders and ceramic powders. The former technique is used for producing low cost and moderate performance composite materials which are potential materials for manufacturing automotive parts, while the latter technique is used to produce high cost but high performance nanocomposites with potential applications in aerospace industry. It has been established that a combination of high energy mechanical milling, thermal treatment is very effective in achieving the desired microstructure and properties. This paper is to provide an overview of the results of a comprehensive study undertaken at Waikato University on the inter-relationships among composition, processing condition, microstructure and properties of the titanium aluminide-ceramic composite materials synthesized using these techniques. Work published in literature on this type of materials will also reviewed. Ways of improving the fracture toughness of the composite materials and their potential applications will be discussed.

10:50 AM
Production of Ti3Al Based Composite Materials using Mechanical Alloying: *Jing Liang*[1]; D. L. Zhang[1]; W. Gao[3]; Z. W. Li[2]; [1]The University of Waikato, Dept. of Matls. & Proc. Eng., PB 3105, Hamilton New Zealand; [2]The University of Auckland, Dept. of Cheml. & Matls. Eng., Auckland, New Zealand; [3]The University of Auckland, Dept. of Cheml. & Matls. Eng., Auckland, New Zealand

Ti3Al based composite powders containing SiC, TiC and other ceramic particulate were produced by using high-energy mechanical milling. The morphology and microstructure of the as-milled powder particles were investigated using X-ray diffraction (XRD) and scanning electron diffraction. Composite structured powder with the ceramic particles incorporated in the metal matrix formed after milling the elemental powder mixture for 2 hours. With increasing the milling time up to 16 hours, the ceramic particle sizes were reduced down to about 200 nm in average. The composite materials were then produced via cold isostatic pressing and vacuum sintering of the as-milled powder. The phases and structures of the composite materials were characterized using XRD, SEM, TEM and compositional analysis using energy dispersive X-ray spectrometer (EDX). It was found that the ceramic phase heavily reacted with the Ti3Al matrix under certain sintering conditions, so the effects of the ceramic type, size and sintering temperature and time on the reactions were studied. In order to lower the sintering temperature required to produce fully dense composite materials, hot isostatic pressing was used in consolidating the as-milled powders. High temperature oxidation resistance of the materials has also been studied. This paper is to present and discuss the results of this study, with the focus on the understanding of the relationships between processing conditions, microstructures and oxidation resistance of the Ti3Al based composite materials.

11:10 AM
Investigation on Fabrication of TiNiCu Shape Memory Alloy from Elemental Powders: Zheng Qifei[1]; Xie Shuisheng[1]; Yuan Guanshen[1]; [1]Beijing General Research Institute for Non-Ferrous Metals, Beijing China

TiNiCu alloy is one of shape memory alloy, which have excellent property and have been really used. It is difficult to get chemical homogeneity for TiNiCu alloys in usual melt-cast production process. The fabrication of TiNiCu shape memory alloy directly from elemental powders was studded. Powders of Ti, Ni and Cu element were mixed and cold pressed to ingot. The ingot was vacuum-sealed in a glass tube and heated in furnace for 0.5-2 hours at the temperature of 900-1050°, then pressed by a pseudo-HIP'ing method at the press of 500-1000MPa and the time of 5-30 second. X-ray analysis of the product show that by this process the powders of Ti, Ni and Cu elements have became to TiNiCu alloy. Effects of parameters on the fabrication of TiNiCu alloy via above method, such as sintering temperature, sintering time, pressure and cold compact density, were studied.

International Symposium on Science and Technology of Interfaces in Honor of Dr. Bhakta Rath: Advanced Materials

Sponsored by: Structural Materials Division, ASM International: Materials Science Critical Technology Sector, Electronic, Magnetic & Photonic Materials Division, Physical Metallurgy Committee, Superconducting Materials Committee, Jt. Mechanical Behavior of Materials, Titanium Committee

Program Organizers: Sreeramamurthy Ankem, University of Maryland, Department of Material & Nuclear Engineering, College Park, MD 20742-2115 USA; I. Ovidko, Russian Academy of Sciences, Institute of Problems of Mechanical Engineering, Laboratory for Theory of Defects in Materials, St. Petersburg 199178 Russia; Chandra Pande, Naval Research Laboratory, Materials Science and Technology Division, Washington, DC 20375-5000 USA; S. Ranganathan, Indian Institute of Science, Department of Metallurgy, Bangalore 560 012 India

Wednesday AM	Room: 617
February 20, 2002	Location: Washington State Conv. & Trade Center

Session Chairs: Ilya Ovid'ko, Institute of Problems of Mechanical Engineering, Russian Academy of Sciences, Lab. for Theory of Defects in Matls., Bolshoj 61, Vas. Ostrov, St. Petersburg 199178 Russia; Donald U. Gubser, Naval Research Laboratory, Matls. Sci. & Tech., Code 6300, Washington, DC 20375 USA

8:30 AM Invited
Interfaces and Stresses in Nanostructured and High-Tc Superconducting Materials: *Ilya Ovid'ko*[1]; [1]Institute of Problems of Mechanical Engineering, Russian Acad. of Scis., Lab. for Theory of Defects in Matls., Bolshoj 61, Vas. Ostrov, St. Petersburg 199178 Russia

This presentation briefly reviews theoretical models that describe the specific structural and behavioral peculiarities of interfaces (intergrain and interphase boundaries) in nanostructured and high-Tc superconducting materials. The special attention is paid to the role of interfaces as sources of stresses and their influence on the properties of nanostructured and high-Tc superconducting materials. In doing so, theoretical models are considered which focus on the following: (i) Interphase boundaries and stress distributions in nanocrystalline films and nano-scale multilayer coatings. Their effects on the protection properties of nanostructured films and coatings. (ii) Grain boundaries and grain boundary defects in nanostructured bulk materials. Their effects on the mechanical behavior of nanostructured materials. (iii) The structure and stress fields of grain boundaries in polycrystalline high-Tc superconductors. The effects of dilatation stresses of interfaces on high-Tc superconductivity in thin-film and bulk cuprates. This work was supported by the Office of US Naval Research, INTAS and Volkswagen Foundation.

8:55 AM Invited
Grain Boundary Effects in High and Low Tc Superconductors: *Chandra Shekhar Pande*[1]; Robert A. Masumura[1]; [1]Naval Research Laboratory, Matls. Sci. & Tech. Div, Code 6325, 3555 Overlook Ave. S.W., Washington, DC 20375 USA

A high critical current capacity is one of the most important properties needed in superconductors used in large scale applications such as electric motors, The role of grain boundaries is the most significant among the many factors that can effect the critical current in these materials. Interestingly, the behavior of grain boundaries is very different in low and high Tc superconductors. We discuss why grain boundaries enhance Jc in low Tc superconductors but it is the elimination of most of the large angle grain boundaries that is most critical for high Tc Superconductors. Specifically, it is the c-axis texture and a-b grain alignment that is important. These results are verified by texture measurements on BSCCO tapes. Current transport properties of these tapes were also measured and correlated with texture parameters. Mathematical models connecting Jc with grain boundaries in both low and high Tc materials are also discussed.

9:20 AM Invited
Concerning Doping, Segregation, Charge, and Stress at the Grain Boundaries of Cuprate High-Temperature Superconductors: *David O. Welch*[1]; [1]Brookhaven National Laboratory, Matls. & Cheml. Scis. Div., ES&T Dept., Bldg. 480, PO Box 5000, Upton, NY 11973-5000 USA

Grain boundaries play a very significant role in the science and technology of high-temperature superconductors. Their effects can be desirable or undesirable, according to the required properties. On the one hand, Josephson junction devices can be fabricated using grain boundaries to form the junctions; on the other hand, great efforts must be made to reduce the deleterious effects of grain boundaries on the attainable critical current density in conductors for electric power applications. The short superconducting coherence lengths, the low carrier density with its sensitivity to stress and disorder, as well as the sensitivity of the metal-insulator transition to these variables, the complex crystal structure and the resulting anisotropy of superconducting properties are all important factors in the structure and the effects of grain boundaries in cuprate superconductors. In this talk I will discuss the thermodynamics and kinetics of these effects, with reference to the available data from transmission electron microscopy and with emphasis on the need for the use of open-system thermodynamics and kinetics, and for consideration of space charges and the effects of low carrier densities and the anisotropy of the layered crystal structure on its screening. I will also discuss the prospects for the use of suitable doping to alleviate the undesirable effects of grain boundaries in cuprates. This research was performed under the auspices of the US Department of Energy, Division of Materials Sciences, Office of Basic Energy Sciences under Contract No. DE-AC02-98CH10886.

9:45 AM Invited
Substituted Yttrium and Rare Earth Iron Garnet Films for Magneto-Opt Devices: *Pragati Mukhopadhyay*[1]; T. Chandra[2]; [1]Advanced Centre for Research in Electronics, Indian Inst. of Tech., Bombay, 4000076 India; [2]University of Wollongong, Dept. of Matls. Eng., Wollongong, NSW 2522 Australia

Garnet films have emerged as promising magneto-optic (MON, materials with good oxidation resistance compared to the more conventional but corrosion/oxidation prone Re-Tm alloy films Substitution of bismuth ion and rare earth ions like Gd, Ce, Pr, Nd, Tb, Lu, Tin, etc are known to enhance the MO activity in rare earth garnets. We report here the magnetic, magneto-optic, (MO) and crystalline properties of Bi- substituted Lutetium, Thulium, Cerium Iron Garnet films (of the type Bi:LuIG, Bi:TmIG, Ce:YIG) epitaxially grown on single crystal Gadolinium Gallium Garnet (GGG) and compare with other substituted rare earth garnet films.

10:10 AM Invited
Melting of Nano-Embedded Particle: The Role of Interface Structure: *Ramasis Goswami*[1]; *David Welch*[2]; *Kamanio Chattopadhyay*[3]; [1]SUNY at Stony Brook, Matls. Sci. & Eng., Stony Brook, NY 11794 USA; [2]Brookhaven National Laboratory, Energy Scis. & Tech. Dept., Upton, NY USA; [3]Indian Institute of Science, Dept. of Metall., Bangalore, Karnataka 560012 India

Melting of nanosized embedded particles have drawn considerable attention in recent time. A considerable amount of superheating is reported in nanoparticles embedded in a matrix. A large superheating of approx. 470K was observed for nanocrystals of Ar embedded in an Al matrix, where the amplitude of vibration of atoms is reported to be depressed at the solid-solid interface. The superheating of nanocrystals of Pb embedded in Zn is attributed to the change in the morphology of the particle which modifies the particle-matrix interface. The presence of epitaxy of closed-packed planes and directions can promote the condition for superheating. The present work reports on the existence of steps at the interface on melting of the nanosized-embedded Bi and Pd particles in different matrices. Experiments have also been carried out to study the influence of the defects like dislocations, introduced at the particle-matrix interface by deformation, on melting. Acknowledgements : We acknowledge the Alexander von Humboldt Foundation and the US Department of Energy, under contact No. DE-AC02-98CH 10 886 of the Energy Sciences and Technology Department, Brookhaven National Laboratory, Upton, NY.

10:35 AM Invited
Interfaces in Soft Materials: *R. Shashidhar*[1]; [1]Naval Research Laboratory, Code 6900, Washington, DC 20375 USA

Soft condensed matter materials like liquid crystals and polymers exhibit unique properties in their thin film state. These properties depend very strongly on the interaction of the materials with surfaces. An example if such interfacial interaction between liquid crystal and solid surface is the ability to orient microscopic liquid crystals using an extremely thin and tailored interface. This talk presents the development of a self-assembling monolayer which, when fabricated on a solid surface, dictates the orientation of liquid crystal molecules, the relation between the interfacial energy, the chemical anisotropy and the properties of liquid crystals. This talk also discusses the prospects of using liquid crystals for imaging the structure of soft interfaces, particularly bio-interfaces.

11:00 AM Invited

Interface Studies in Quasicrystalline Al–Cu–Fe and Al–Pd–Mn Alloys: R. Divakar[1]; V. S. Raghunathan[1]; *S. Ranganathan*[2]; [1]Materials Characterisation Group, Indira Gandhi Ctr. for Atomic Rsrch., Kalpakkam 603102 India; [2]Centre for Advanced Study, Dept. of Metall., Indian Inst. of Sci., Bangalore 560012 India

The structural characterization of interfaces in quasicrystalline systems has been of interest for some time now. Characterization of interfaces in these materials is of particular interest with respect to the known structural relations between the quasicrystalline phases and the coexisting crystalline phases. High-resolution transmission electron microscopy (HREM) has been a technique of choice for these studies. In the present paper, the status of experimental results on the structure of interfaces in quasicrystalline systems is reviewed. In addition, our results of the experimental investigation of interfaces in Al–Cu–Fe and Al–Pd–Mn are systems are reported. In both systems, coexisting crystalline phases are found that are structurally related to the icosahedral quasicrystals. Thus, in addition to the variability of interfaces with respect to structure, composition and orientation of the grains, translational order also change across an interface. Two classes of interfaces have been studied in these systems. The first is the interface between icosahedral phase grains. In Al-Cu-Fe, quasicrystal–quasicrystal interfaces show a high degree of curvature with frequent, irregularly spaced ledges that are atomically flat with little disorder. For the second class of interfaces, similar interfacial structures have been observed at interfaces between the icosahedral phase and the related crystalline phase where the interfacial plane corresponds to the common symmetry axis shared by the two phases, in both Al–Cu–Fe and Al–Pd–Mn systems. The observed special features of grain boundaries and ledge interfaces are discussed in terms of common structural motifs and the resulting orientation relation between the quasicrystalline and related crystalline phases.

Lead-Free Solders and Materials Issues in Microelectronic Packaging: Mechanical Properties, Fatigue and Creep

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

Program Organizers: Srini Chada, Motorola, Department APTC, Fort Lauderdale, FL 33322 USA; Darrel R. Frear, Motorola, Tempe, AZ 85284 USA; Sung-Ho Jin, Lucent Technologies, Bell Laboratories, Murray Hill, NJ 07974 USA; Sung Kang, IBM, T. J. Watson Research Center, Yorktown Heights, NY 10598 USA; C. Robert Kao, National Central University, Department of Chemical Engineering, Chungli City, Taiwan; Michael J. Pfeifer, Motorola, Northbrook, IL 60062 USA; Martin Weiser, Honeywell Electronics Materials, Plated and Discrete Products, Spokane, WA 99216 USA

Wednesday AM	Room: 612
February 20, 2002	Location: Washington State Conv. & Trade Center

Session Chairs: Sungho Jin, Bell Labs, Agere, 600 Mountain Ave., Murray Hill, NJ 07974 USA; Carol Handwerker, NIST, Metall., Gaithersburg, MD USA

8:30 AM Invited

A Constitutive Model for Predicting Thermal Mechanical Fatigue in Low-Temperature, In-Sn Solder Interconnects: *Paul T. Vianco*[1]; Jerome Rejent[1]; Arlo Fossum[1]; Michael Neilsen[1]; [1]Sandia National Laboratories, PO Box 5800, MS 0889, Albuquerque, NM 87185-0889 USA

The interest in low-temperature, In-based solders has stemmed satellite/space applications as well as cryogenic service. A study was performed to develop the constitutive model for the Pb-free solder, 52In-48Sn (wt.%). Compression stress-strain tests determined the yield stress and static elastic modulus values at -25°C, 25°C, 75°C, and 100°C. Yield stress values ranged from 17 MPa at -25°C to 1.32 MPa at 100°C. The static elastic modulus ranged from 1.6 GPa (-25°C) to 0.3 GPa (100°C). Compression creep behavior exhibited an apparent activation energy of 55 kJ/mol and stress term exponent of 1.7. Sandia is a multiprogram laboratory operated by Sandia Corporation, A Lockheed Martin Company, for the US Dept. of Energy under Contract DE-AC04-94AL85000.

8:55 AM

Low Cycle Fatigue Life of Lead-Free CSP/PWB Interconnects: *Yoshiharu Kariya*[1]; Tomoo Morihata[1]; Yasunori Tanaka[2]; Masahisa Otsuka[1]; [1]Shibaura Institute of Technology, Matls. Sci. & Eng., 3-9-14 Shibaura, Minato-Ku, Tokyo 1088548 Japan; [2]NEC Corporation, Mobile Terminal Div., Ikebe-cho, Tsuzuki-Ku, Yokohama, Kanagawa 224 Japan

With increasing of the production volume of fine pitch BGA type packages such as CSP, a demand on the establishment of the reliability evaluation for BGA/PWB (Printed Wiring Board) joints is increasing. Especially, the shear fatigue properties of the joints made up using lead-free solders are great interest. However, the shear fatigue data of actual BGA joints very limited, as the fatigue test requires fine displacement or load control ability of the test machine. In this study, the straddle board fatigue test using a conventional servo-valve-controlled electro-hydraulic testing machine has been performed to look for strain-life relationship of real lead-free CSP/PWB interconnections. The fatigue life was correlated to inelastic displacement divided from hysteresis loop by a pseudo Coffin-Manson's law. The difference in the fatigue lives of 0.8mm pitch and 0.5mm pitch CSP will be presented. The comparison between the bulk data and the joint data also will be presented.

9:15 AM

Modeling Thermomechanical Fatigue Behavior of Sn-Ag Solder Joints: *J. Lee*[1]; H. Rhee[1]; K. N. Subramanian[1]; T. R. Bieler[1]; J. P. Lucas[1]; [1]Michigan State University, Dept. of Matls. Sci. & Mech., 3536 Engineering Bldg., E. Lansing 48824-1226 USA

Stresses that develop due to CTE mismatches between the solder/substrate/components contribute to the TMF of solder joints. However, the relative importance of the several processes that contribute to the observed damage accumulation and their role in affecting the reliability of the solder joint are far from being understood. Processes such as aging, creep/stress relaxation, and stress reversals are some of the important processes. These factors are affected by service conditions such as the temperature extremes experienced, rates of heating/cooling, dwell times at the extreme temperatures, etc. These preliminary efforts to model TMF in Sn-Ag solder joints will focus on the findings of the role of each of these parameters and their inter-relationships. Acknowledgment: This project is funded by National Science Foundation under grant NSF-DMR-0081796.

9:35 AM

The Vibration Fracture Characteristics of Sn-Ag Lead-Free Solders: *Chiang Ming Chuang*[1]; [1]National Cheng Kung University, Matls. Sci. & Eng., Tainan 701 Taiwan

The research has two aspects; one is the different solidification rate, putting Sn-3.5wt%Ag alloy in different cooling-rate mold. And other is variation of Ag content from 3.5 to 6.0wt%. The experimental results show that the vibration-fracture resistance of lower cooling-rate and higher Ag content specimens is better than higher cooling-rate and lower Ag content specimens. Comparing to near eutectic Sn-Pb solder, Sn-Ag samples have better vibration properties for they possesses a smaller initial deflection amplitude under the same vibration push force and higher crack propagation resistance under the same initial deflection amplitude. Differing vibration-fracture resistance could be correlated with differing crack-propagation behavior.

9:55 AM

High Temperature Mechanical Properties of the Lead-Free Sn-3.5Ag-xCu Alloys: *S. W. Shin*[1]; D. K. Joo[1]; Jin Yu[1]; [1]Korea Advanced Institute of Science and Technology, Ctr. for Elect. Pkgg. Matls., 373-1 Kusong-dong, Yusong-gu, Daejon 305-701 Korea

In the electronics industry worldwide, using lead-free solders is becoming more mandatory recently, and Sn-3.5Ag based ternary alloys with Cu are strong candidate materials. On that regard, substantial amounts of work on various properties of Sn-3.5Ag based alloys are under way. However, high temperature mechanical creep data of the Sn-3.5Ag alloys, including the effects of the solder microstructure, cooling rate and ball size, are rather rare in literature. In the present work, Sn-3.5Ag-xCu alloys with five different levels of Cu (0, 0.5, 0.75, 1.0, 1.5wt%) and a Sn-0.7Cu alloy were prepared. Conventional creep tests using rolled and stabilized bulk specimens were conducted in order to understand the creep mechanism of the alloys under the stable microstructure, while lap shear tests with reflowed solder balls of varying size were conducted to simulate the creep deformation of solders under the real package situation. The latter usually involves the effects of the intermetallic formation at the solder/die pad interface. Since the creep deformation depends on the microstructure of the reflowed solder which varies with the ball size, as-cast bulk specimens with the same microstructure as the reflowed solder balls of varying size were prepared by controlling the cooling rate, and their creep behaviors were compared with those of the lap shear and the as-stabilized bulk specimens. Result show that the creep strength were best with 0.75~1wt% Cu and the creep exponent was ~4 with the nucleation and growth of creep voids at the grain interior. Results also indicate substantial differences among creep behaviors of the as-stabilized bulk, reflowed solder, and as-cast bulk with the microstructure of the reflowed solder specimens.

10:15 AM Break

10:30 AM Invited
Damage Accumulation under Repeated Reverse Stressing of Sn-Ag Solder Joints: *K. C. Chen*[1]; K. N. Subramanian[2]; [1]California Polytechnic State University, Matls. Eng. Dept., San Luis Obispo, CA 93407 USA; [2]Michigan State University, Dept. of Matls. Sci. & Mech., 3536 Engineering Bldg., E. Lansing, MI 48824-1226 USA

Sn-Ag solder joints were subjected to repeated reversed stress under constant strain amplitude conditions. Effects of strain amplitude, strain rate, hold times at the stress extremes, solder joint thickness, and temperature were investigated. The role of constraints present in the joint on the Bauschinger effect and on damage accumulation was also evaluated. Microscopic studies indicate significant amount of damage arising from grain boundary sliding and grain separation (decohesion) as a result of repeated stress. Implications of the findings from this study to electronic solder joints will be presented. Acknowledgment: The authors thank the National Science Foundation for providing financial support for this project as additional funding to NSF grant NSF-DMR-0081796.

10:55 AM
A High Creep Resistance Tin-Based Alloy for Soldering Applications: *Rodney J. McCabe*[1]; Morris E. Fine[2]; [1]Los Alamos National Laboratory, MST-8, MS-G755, Los Alamos, NM 87545 USA; [2]Northwestern University, Matl. Sci. & Eng., 2225 N. Campus Dr., Evanston, IL 60208 USA

Soldering applications such as optical interconnects require dimensionally stable solders because any creep deformation may result in device degradation or failure. Using comparatively simple processing steps, tin-based alloys strengthened by the precipitate SbSn were found to possess excellent creep resistance below 100°C compared to other soldering alloys. The creep properties of these alloys were found to be relatively unaffected by aging at temperatures up to 100°C for as long as 8 weeks. These alloys owe their strength to an advantageous array of high aspect ratio SbSn whiskers crisscrossing in five crystallographic directions. This configuration results in a composite strengthening effect that is a function of particle size, spacing, and volume fraction.

11:15 AM
Effect of Cooling Rate on the Tensile Behavior of Pb-Free Solders: *Felipe Ochoa*[1]; George Piotrowski[1]; Jason Williams[1]; Nikhilesh Chawla[1]; [1]Arizona State University, Dept. of Cheml. & Matls. Eng., Tempe, AZ 85284 USA

The mechanical behavior and microstructure of bulk, pure solders as a function of cooling rate was studied. Scanning and transmission electron microscopy were used to characterize the effect of cooling rate on solder microstructure. Thermal aging studies on solder joints, also as a function of cooling rate, were conducted and the evolution of intermetallic growth was characterized. Solder fracture surfaces were charaterized to elucidate the synergistic relationship between mechanical behavior and microstructure. Research sponsored by the National Science Foundation under contract# DMR-0092530 (Dr. K. L. Murty, Program Manager).

11:35 AM
Creep Behavior of Sintered Solder Joints: *Mark A. Palmer*[1]; Nicole S. Erdman[1]; [1]Kettering University, IMEB Dept., 1700 W. Third Ave., Flint, MI 48504-4989 USA

Low-flux lead-free composite solder joints have been shown to have mechanical properties comparable to reflowed eutectic tin-lead solder joints. However, before such materials can be fully considered as a low-temperature processing alternative the creep behavior of such materials must be understood. The creep behavior of composite Sn-Ag-Bi and Sn-Ag-Cu will be evaluated at high fractions of the measured yield stress and high fractions of the sintering temperature. This work is funded by the National Science Foundation's Environmentally Benign Manufacturing Program.

11:55 AM
Creep and Microstructure of Lead-Free Solders: *Vladimir Igoshev*[1]; Jacob Kleiman[2]; [1]Research in Motion, 295 Phillip St., Waterloo, ON N2L 3W8 Canada; [2]Integrity Testing Laboratory, 80 Esna Park Dr., Units 7-9, Markham L3R 2H7 Canada

A critical review of data on activation energy of creep for three lead-free solders is presented. The review indicates that a large scatter exists in the data. In order to explain the discrepancy, an assumption was made that such fracture processes as nucleation, accommodation and propagation of pores/cracks take place in an earlier stage of creep. These processes will play a significant role during creep deformation of lead-free solders and should be taken into consideration to calculate the value of true, not apparent activation energy of creep. Creep experiments conducted on bulk Sn-3.5%Ag solder alloy and solder coupons (Cu coupons soldered with the alloy) confirmed that nucleation of cracks in the solder occurs after a testing time of $t = 0.2t_c$, where t_c is the specimen lifetime.

Magnesium Technology 2002: Magnesium Wrought Products–A Session in Memory of William A. Barnes

Sponsored by: Light Metals Division, Magnesium Committee, International Magnesium Association
Program Organizers: Howard I. Kaplan, Magnesium Corporation of America, Salt Lake City, UT 84116 USA; Menachem Bamberger, Technion, Israel Institute of Technology, Haifa 32000 Israel; Byron B. Clow, International Magnesium Association, McLean, VA 22101 USA; Gerald S. Cole, Ford Motor Company, Ford Research Laboratories, Dearborn, MI 48121 USA; Rod Esdale; John N. Hryn, Argonne National Laboratory, Argonne, IL 60439-4815 USA; Zi-Kui Liu, Pennsylvania State University, Materials Science and Engineering, University Park, PA 16082-5005 USA; John L. Mihelich, Metal Experts International, Winston, GA 30187 USA; Ramaswami Neelameggham, Magnesium Corporation of America, Salt Lake City, UT 84116 USA; Eric A. Nyberg, Pacific Northwest National Laboratory, Materials Processing Group, Richland, WA 99352 USA; Mihriban O. Pekguleryuz, Noranda, Noranda Technology Centre, Pointe-Claire, Quebec H9R 1G5 Canada; Bob R. Powell, General Motor Corporation, NAO Research and Development Center, Warren, MI 48090-9055 USA; Allen Schultz, Hatch, Mississauga, Ontario L5K 2R7 Canada

Wednesday AM	Room: 606
February 20, 2002	Location: Washington State Conv. & Trade Center

Session Chairs: Darryl Albright, Hydro Magnesium, Magnesium Mkt. Dvlp., 39209 Six Mile Rd., Ste. 200, Livonia, MI 48152 USA; Henry J. Rack, Clemson University, Sch. of Cheml. & Matls. Sci., 208 Rhodes Hall, Clemson, SC 29634-0921 USA

8:30 AM Opening Remarks
William A. Barnes–A Dedication

8:40 AM Invited
Magnesium Wrought and Fabricated Products–Yesterday, Today, and Tomorrow: *Robert Brown*[1]; [1]Magnesium Monthly Review

The developers of magnesium metal production were always interested in methods of producing alloys and products. Casting was the first major development, but it was closely followed by rolling, forging and extrusion. This paper will review the tremendous historical developments in wrought products during the 1930's in Germany and during the 1940's and after in the US and Great Britain. At the peak of wartime production, thousands of tons of magnesium sheet were produced each month and used in aircraft in many areas. Aircraft of all magnesium, extrusions and sheet and castings were made by the Germans (Arado 196) and the US, XP56 and F-80. The US produced B-36 had 19,000 pounds on each aircraft, including a large amount of sheet for the pressurized fuselage. Most of the magnesium sheet were produced on rolling mills developed for other metals until Dow built the large magnesium fabrication facility at Madison, Illinois. (Owned and operated by Spectrulite). In the 1950's, Brooks and Perkins began to develop magnesium rolling and eventually had two rolling mills. They also were instrumental in building the primary magnesium reduction plant in Selma, Alabama to reduce their dependence on Dow for magnesium. The rapid expansion and development of rolling and forging will be discussed and contrasted to the present day experiments and testing. Included will be a discussion of the twin roll casting operations proposed by Magwerkes in 1988-89.

9:10 AM
Relation between Microstructure and Mechanical Properties in Magnesium Wrought Alloy AZ31: *Dietmar Letzig*[1]; Jan Bohlen[1]; Heinz-Günther Brokmeier[2]; Andrzej Styczynski[3]; Christian Hartig[3]; Karl-Ulrich Kainer[1]; [1]GKSS Forschungszentrum GmbH, Zentrum für Magnesiumtechnologie, Max Planck Str., Geesthacht 21502 Germany; [2]TU Clausthal, GKSS-Hochschulgruppe, Max-Planck-Str., Geesthacht 21502 Germany; [3]TU Hamburg Harburg, Werkstoffphysik/Technologie, Eißendorfer Str. 42, Hamburg 21073 Germany

Magnesium wrought alloys as light weight materials offer a high potential for industrial structural applications. However, due to the basic hexagonal lattice structure magnesium alloys show poor mechanical properties and formability. In order to improve the mechanical properties the influence of the microstructure on the deformation behaviour is of fundamental interest. The processing of wrought materials itself influences the microstructure and thus the mechanical properties. The relation between process parameters and microstructure is therefore of interest for the development and improvement of industrial applicable magnesium wrought alloys. Using alloy AZ31 the process conditions of extruded bars and rolled sheets are characterized and compared in order to determine the effect of the microstructure on deformation mechanisms. Microstructural evaluations, texture measurements and mechanical properties are presented.

9:35 AM
Plastic Anisotropy in Magnesium Alloy AZ31B Sheet: *Sean R. Agnew*[1]; [1]University of Virginia, En-Matl. Sci./Eng. Dept., PO Box 400745, Thornton Hall, B120, Charlottesville, VA 22904-4745 USA

It is well established that crystallographic texture induced plastic anisotropy in sheet metal can give rise to a variety of formability problems. The earing behavior of deep drawn aluminum beverage cans is a classical example. Interest in the application of lightweight magnesium alloys has been growing over the past decade. One problem facing the application of wrought magnesium alloys, in particular, is their poor cold forming properties. Historically, this has been linked with an inadequate number of independent slip systems within magnesium's hexagonal crystal lattice. An issue that has received less attention is the impact of the strong crystallographic texture induced during primary forming operations, such as rolling, upon subsequent forming steps, such as sheet stamping. Measurements of the R-value for 0, 45, and 90° oriented tensile samples have highlighted a strong in-plane anisotropy, R(0°)~1 and R(90°)~4. Simulations using the viscoplastic self-consistent model have been used to link crystallite level plastic anisotropy with the macroscopic properties. This information may be used to explain the poor sheet forming behavior of magnesium alloys and offer insights for potential solutions to the problem.

10:00 AM
Elevated Temperature Behavior of Sheet Magnesium Alloys: *Paul E. Krajewski*[1]; [1]General Motors Corporation, R&D Ctr., 480-106-212, 30500 Mound Rd., Warren, MI 48090 USA

The mechanical behavior of three commercially available magnesium sheet materials was investigated at temperatures between 300ºC and 500ºC. The three materials, AZ31B-O, AZ31B-H24, and AZ61A-O, all showed significant improvements in total elongation at strain rates between 0.001/sec and 0.01/sec. AZ31B-H24 exhibited a total elongation of over 400% at temperatures above 450ºC. The dominant failure mechanism underwent a transition from cavitation controlled fracture, to necking controlled fracture in this temperature/strain rate regime. The transition from cavitation to necking dominated failure was evaluated microstructurally and the results were related to total elongation.

10:25 AM Break

10:45 AM
Grain Refinement under Warm Deformation of Magnesium Wrought Alloy ZK60: R. Kaibyshev[1]; *A. Galiyev*[1]; G. Gottstein[2]; [1]Institute for Metals Superplasticity Problems, Khalturina 39, Ufa 450001 Russia; [2]Institut fur Metallkunde und Metallphysik, RWTH Aachen, Aachen D-52056 Germany

The possibility of producing an ultrafine-grained structure in magnesium alloy was considered. The coarse-grained Mg-5.8%Zn-0.65%Zr alloy was examined. Compression tests were carried out in air at a temperature of 423K and at a fixed strain rate of $2.8x10^{-3}$ s^{-1}. It was shown that formation of new grains took place during warm deformation. Almost full-recrystallized structure with an average grain size of 0.8μm was evolved after large cumulative strain. The main feature of recrystallized structure was highly non-equilibrium grain boundaries, which were sources of internal long-range stress fields. It was suggested that the structural changes were connected with operation of a specific type of dynamic recrystallization defined as low temperature dynamic recrystallization (LTDRX). The mechanism of ultrafine-grained structure formation under warm deformation was discussed in terms of LTDRX.

11:10 AM
Direct and Indirect Extrusion of AZ 31: *Klaus B. Müller*[1]; [1]Technische Universität Berlin, Forschungszentrum Strangpressen, Gustav-Meyer-Allee 25, Sekr.TIB 4/1-2, Berlin D-13355 Germany

The paper describes the results of direct and indirect extrusion of the magnesium alloy AZ 31. The trials were carried out on the 8 MN horizontal extrusion press of the r&d center of extrusion. Both extrusion procedures, direct and indirect, are possible. The press unit is equipped with load cells to record the total force F(T), friction force F(F) and die force F(D), whereby friction force F(F) only occurs during direct extrusion. Programmable logical controllers offer a broad margin for development. By means of a computer-aided measuring system, forces can be determined in relation to the ram displacement. The important advantage of indirect extrusion is the absence of friction between billet and container. This ensures a largely homogenous flow of the material and an important decrease of required total extrusion force. Trials were done by different temperatures and extrusion speeds.

11:35 AM
The Hot Working Flow Stress and Microstructural Evolution of Wrought Magnesium Alloy AZ31: *Aiden G. Beer*[1]; Matthew R. Barnett[1]; [1]CRC for Cast Metals Manufacturing (CAST), Deakin University, Sch. of Eng. & Tech., Pigdons Rd., Geelong, Victoria 3217 Australia

The evolution of hot working flow stress and microstructure for wrought magnesium alloy AZ31 was characterised. Torsion and compression testing, at temperatures between room temperature and 450°C and strain rates between and 0.01s-1 to 1s-1, was employed to determine the influence that these variables have on flow stress and microstructural development. Constitutive equations were developed for the peak and steady-state flow stresses. Optical observations revealed twinning and dynamically recrystallised (DRX) grains. The latter were observed at test temperatures of 200°C and above. The influence of strain rate and temperature on the dynamically recrystallised grain size was quantified for samples that displayed more than 25% dynamic recrystallisation. The flow stress at low strains was found to be strongly dependent on texture and deformation mode. This can be described in terms of the influence of the deformation accommodating processes of prismatic slip, twinning and DRX. At higher strains, the flow stress was relatively insensitive to deformation mode and initial texture.

Materials Processing Fundamentals - III

Sponsored by: Extraction & Processing Division, Process Fundamentals Committee
Program Organizers: P. N. Anyalebechi, Grand Valley State University, Padnos School of Engineering, Grand Rapids, MI 49504-6495 USA; Adam Powell, Massachusetts Institute of Technology, Cambridge, MA 02139-4301 USA

Wednesday AM — Room: 614
February 20, 2002 — Location: Washington State Conv. & Trade Center

Session Chairs: Ramana G. Reddy, University of Alabama, Metall. & Matls. Eng., A129 Bevil Bldg., 126 7th St., Tuscaloosa, AL 35487-0202 USA; Patrick R. Taylor, University of Tennessee, Metlgcl. Eng., 1010 W. Cayuse Dr., Knoxville, TN 37996 USA

8:30 AM
Computer Modelling of Rotary Furnaces: A Lumped Parameter Approach: *Ian Masters*[1]; [1]University of Wales-Swansea, Mechl. Eng., Singleton Park, Swansea SA2 8PP UK

Rotary furnaces are widely used throughout the metals industry. These furnaces vary in size and geometry, but are fundamentally the same from a thermodynamic viewpoint. A generic method is proposed that can be used to model all furnaces of this type, provided that the correct material and process parameters are known. Previous work has been based on a continuum (FEA or CFD) approach. However, the complex fluid/solid interactions present in a rotary vessel are not easily solved using these methods, which work best where the material boundaries are well defined. In this paper a lumped parameter model is proposed. Variations within a section of the model are ignored, but to ensure thermodynamic correctness, the heat transfer between sections is carefully considered. For example, it is reasonable to assume that the whole of the melt pool is at the same temperature, due to rotary mixing. This may then be modelled with a single set of parameters, and the detail is contained in obtaining the correct heat transfer mechanisms from the rest of the furnace.

9:00 AM
Investigation of the Al Ball Plug/319 Al Casting Hole Press-Fit System: W. Kasprzak[1]; J. H. Sokolowski[1]; *D. Szablewski*[1]; [1]NSERC/Ford-Nemak/University of Windsor, Mech., Autom. & Matls. Eng., Rm. 203, Essex Hall, 401 Sunset Ave., Windsor, ON N9B 3P4 Canada

Press-fit systems are widely used to seal oil lines in automotive engine components. In the case studied a ball plug made from an Al alloy was inserted into a 319 Al alloy cast component. The oil lines were subjected to the required component service pressure. This paper addresses the analysis of the ball plug/casting hole press-fit performance. The tools used to investigate the plug system included: SEM/EDS technique for the assessment of the plug and casting hole wall surface integrity, Image Analysis methods for the characterization of the ball plug/casting hole interface, matrix microhardness measurements of the plug and casting components, laboratory ball plug insertion and pressure tightness tests, as well as identification of the leaking mechanisms present in the system. Laboratory tests indicated that optimization of the aluminum matrix hardness in the 319 Al alloy cast component resulted in considerable improvement of the sealing properties.

9:30 AM
Evaluation of Field Activated Sintering of Silicon: *Martin Kraemer*[1]; Joanna R. Groza[1]; [1]University of California, Chem. Eng./Matl. Sci. Dept., One Shields Ave., Davis, CA 95616 USA

A kinetic study on sintering pure, fine grained silicon powder by field activated sintering using the Sumitomo SPS sintering system has been carried out. Densities better than 97% could be achieved by tailoring temperature and pressure profiles. Densification kinetics as a function of different heating rates and uniaxial pressures have been determined to derive experimental values for activation energies. The results are discussed in terms of kinetics and the technical capabilities and potential of the sintering system addressing both problems of temperature distribution throughout the specimen and furnace setup which have been studied by finite element modeling and experiments.

10:00 AM Break

10:30 AM
Rotating Disk Studies of Iron Reactions in Water under Abiotic and Biotic Conditions: *Batric Pesic*[1]; [1]University of Idaho, Matls. Sci. & Eng., COMER-McClure, Moscow, ID 83844-3024 USA

The iron reactions with water were examined under abiotic and biotic conditions by using pure iron in a rotating disk technique. The biotic conditions were produced by utilizing harvested cells of Thiobacillus ferrooxidans. The parameters studied were: pH, rotation speed, bacterial cells concentration, and concentration of oxygen. The reactions of iron were studied by measuring the rate of iron dissolution and by electrochemical techniques. It was found that iron reactions with water were mostly independent of all parameters studied except of the concentration of oxygen. In addition, the iron dissolution data and the results from electrochemical experimentation will also be correlated to the morphology of surface reaction products, which was done by atomic force microscopy.

11:00 AM
Magnetic Properties of Undercooled Co-Based Alloys Measured by Means of a Faraday-Balance: *Sven Reutzel*[1]; Dieter M. Herlach[1]; [1]German Aerospace Center, Inst. of Space Simulation, Linder Hoehe, Cologne 51170 Germany

Investigations show that Co-based melts embedded by glass flux in a crucible can be undercooled nearly as strong as samples processed containerlessly by electromagnetic levitation. This allows to measure magnetic susceptibility on undercooled melts while combining the faraday method with undercooling technique. The magnetic susceptibility of Co and Co-based alloys (such as Co-Cu, Co-Pd, Co-Au) is analysed as a function of temperature from superheated to undercooled state. This is done by measuring the change of magnetic force FZ on a sample in a constant magnetic field B0 and an additional gradient field by means of a faraday-balance. When liquid Co-based alloys are undercooled the magnetisation steeply rises if temperature approaches the Curie-temperature. The magnetisation is measured for some Co-based alloys in liquid state as function of alloy system and its concentration. The results show that the magnetic susceptibility of the liquid undercooled samples follows a Curie-Weiss behaviour, from which Curie-temperature and magnetic moments are inferred.

11:30 AM
Potentiostatic Leaching Kinetics of Pyrite/Marcasite in Sterile Acid Ferric Sulfate Media: *Sylvie C. Bouffard*[1]; David G. Dixon[1]; [1]The University of British Columbia, Dept. of Metals & Matls. Eng., 309-6350 Stores Rd., Vancouver, BC V6T 1Z4 Canada

Abstract unavailable

12:00 PM
The Effect of Tap Water and Selected Anions on the Corrosion of Copper: *M. A. Llavona*[1]; B. Diaz[1]; A. M. Fernandez[1]; M. C. Garcia[1]; J. L. Ibanez[1]; N. Velasco[1]; R. Zapico[1]; [1]University of Oviedo, Dept. of Matls. Sci., US Mining & Topographic Engineering, Reinerio Garcia s/n, 33600, Mieres Spain

For several decades, numerous researchers have tried to artificially prepare Patinas in different metals, using diverse procedures. In some of these, immersion methods were proposed, controlling the type of solution, concentration, pH, temperature and time. In other procedures, different types of paints or varnishes were applied. The development of an artificial process to create copper Patina supposes an important success on the market as it is a product which is being demanded by the promoters because of both the added value and the aesthetic outlook of the buildings.

Materials & Processes for Submicron Technologies - II: Materials & Processes for Microelectronic Devices

Sponsored by: Electronic, Magnetic & Photonic Materials Division, Thin Films & Interfaces Committee
Program Organizers: Seung H. Kang, Lucent Technologies, Orlando, FL 32819 USA; N. (Ravi) M. Ravindra, New Jersey Institute of Technology, Department of Physics, Newark, NJ 07102-1982 USA

Wednesday AM	Room: 209
February 20, 2002	Location: Washington State Conv. & Trade Center

Session Chairs: Mahesh K. Sanganeria, Novellus Systems; Sailesh M. Merchant, Agere Systems, VLSI Process Dvlp.; Nuggehalli M. Ravindra, New Jersey Institute of Technology, Dept. of Phys., 161 Warren St., Newark, NJ 07102-1982 USA

8:30 AM Invited
Recent Developments in Rapid Thermal Processing: *Anthony T. Fiory*[1]; [1]New Jersey Institute of Technology, Dept. of Phys., Newark, NJ 07012 USA

Complementary metal-oxide semiconductor Si processing uses rapid thermal annealing with a short dwell time at maximum temperature to reduce the diffusion of implanted dopants in the formation of shallow junctions and for high electrical activation of dopants in polycrystalline Si gate electrodes. Advanced methods use "spike anneals," wherein high temperature-ramp rates are used for both heating and cooling, while also minimizing the dwell time at peak temperature to nominally zero. The fast thermal cycles are required to reduce the undesirable effects of transient enhanced diffusion and thermal deactivation of the dopants. Original methods for single-wafer heating by incandescent or electric arc lamps, or by a steady heat source with rapid wafer transfer, have been refined for mass production of integrated circuits. Since junction profiles are sensitive to annealing temperature, the challenge in spike annealing is to maintain temperature uniformity across the wafer and repeatability from wafer to wafer. Multiple lamp systems use arrayed temperature sensors for individual control zones. Other methods rely on process chambers that are designed for uniform wafer heating. Generally, sophisticated techniques for accurate temperature measurement and control by emissivity-compensated infrared pyrometry are required, since processed Si wafers exhibit appreciable variation in emissivity.

9:00 AM
Integration Issues in the Development of Poly-Metal(W/WN/Poly Silicon) Gate using 0.15µm DRAM Technology: *Jun Ho Choy*[1]; Byung Hak Lee[1]; Chang Ki Kwan[1]; Jae Hyung Kim[1]; Tae Keun Hwang[1]; Yeong Cheol Kim[2]; Joo Chul Park[1]; [1]Hynix Semiconductor, Inc., R&D Div., 1 Hyangjeong-dong, Hungduk-gu, Cheongju, Chungbuk

361-725 Korea; [2]Korea University of Technology and Education, Dept. of Matls. Eng., Chonan, Chungnam Korea

Poly-metal(W/WN/poly silicon) gate process has been successfully developed and integrated using 0.15µm technology for the first time, in an effort to reduce RC delay for giga bit DRAMs. This paper summarizes the problems in the process incompatibility with respect to the conventional polycide(WSix/poly silicon) gate process, device and circuit performances, and the product performance of the fully working 256Mbit DRAM samples employing poly-metal gate. In the integration, the main focus was on the search of a new cleaning chemical for post gate etch process, which is directly related to tungsten contamination. The AC characterization of the circuit revealed the anomalous decay of an electrical signal as it proceeds through the inverter delays. The phenomenon may be explained by the presence of parasitic capacitance in the gate electrode. A solution to this problem was found by experiments employing several different deposition schemes for tungstgen and poly-silicon. The physical characterization on this problem is also addressed. Finally, the examination on the data retention characteristics shows a result quite comparable to that obtained from the samples using conventional polycide gate.

9:20 AM Invited
An Overview of Interdiffusion Phenomena in Ternary Systems–Unusual Diffusion Paths and Diffusion Structures: *M. A. Dayananda*[1]; [1]Purdue University, Sch. of Matls. Eng., W. Lafayette, IN 47907 USA

Interdiffusion in multicomponent systems is reviewed with emphasis on the determination of interdiffusion fluxes and assessment of diffusional and thermodynamic interactions among the diffusants. Selected diffusion phenomena such as uphill diffusion and development of zero-flux planes for individual components are illustrated with specific examples in selected ternary metallic and intermetallic phases and silicide systems. Unusual diffusion structures and diffusion paths experimentally observed for single phase and multiphase diffusion couples in Cu-based and Fe-based ternary systems as well as in selected ternary aluminides and silicides are presented and discussed in the light of uphill diffusion, zero-flux planes and flux reversals, demixing of phases, and variation of diffusion coefficients with composition.

9:50 AM
Transient Enhanced Diffusion in Shallow Junction Formation: *Anthony T. Fiory*[1]; Samrat Chawda[1]; Sridhar Madishetty[1]; Vishal Mehta[1]; N. M. Ravindra[1]; [1]New Jersey Institute of Technology, Dept. of Phys., Newark, NJ 07102 USA

Shallow junctions are formed in silicon for CMOS devices by low-energy ion implantation of B, P, or As species and spike thermal annealing. Boron enhanced transient diffusion, which occurs at high surface concentrations of B, is associated with an excess population of Si interstitials. Rapid thermal annealing with ramp rates of 100 C/s or greater, and nominally zero dwell time at the maximum temperature, denoted as spike annealing, is shown to improve electrical activation while minimizing the diffusion. A similar transient diffusion also occurs in the case of P implantation, where modeling by coupled P-Si diffusion indicates an excess Si-interstitial population of 6 to 10% of the implanted P dose. The electrically-activated fraction of implanted dopant depends mainly on temperature for B species, while for P species it depends on both temperature and P dose. The relatively small diffusion associated with As implants is favorable for shallow junction formation with spike annealing.

10:10 AM Break

10:30 AM
Copper/Low-k Metallization for Semiconductor Devices: *Sailesh M. Merchant*[1]; Seung H. Kang[1]; Mahesh Sanganeria[2]; Bart van Schravendijk[2]; Tom Mountsierb[2]; [1]Agere Systems, VLSI Proc. Dvlp., 9333 S. John Young Parkway, Orlando, FL 32819 USA; [2]Novellus Systems, 3970 N. First St., San Jose, CA 95134 USA

Copper/low-k dielectric materials have been rapidly replacing conventional Al-alloy/SiO2-based interconnects for the fabrication of today's semiconductor devices. This paper reviews the advantages of transitioning to Cu/low-k interconnects. Materials and process challenges during the fabrication of devices with Cu/low-k interconnects are discussed. Reliability concerns associated with such devices are highlighted.

10:50 AM Invited
Low-k Materials Integration Challenges in High Performance Interconnects: *Andrew J. McKerrow*[1]; [1]Interconnect Process, Equipment & Materials, Silicon Tech. Rsrch., Texas Instruments Inc., 13570 N. Central Expressway, MS 3700, Dallas, TX 75243 USA

Abstract unavailable

11:20 AM
Computer Controlled Reactive Ion Plasma Dry Etching of MRAM Stacks: *Todd Scott*[1]; R. B. Young[1]; Keith Prisbrey[1]; [1]University of Idaho, Matls. & Metlgcl. Eng., Moscow, ID 83844-3024 USA

MRAM technology is the next step in computer chip manufacturing. Effectively etching the material without degrading the magnetic properties is a complicated process. 2-micron diameter holes were dry etched in a grid pattern in a Fe/Co/Cu thin film deposited on a silicon wafer. The vertically and undercutting of the holes were measured under SEM, AFM and optical microscopes. The stack's magnetic properties are then characterized. Computer control was necessary to alter the operating parameters online during etching as the reaction progressed through different layers. Spectrometers, electrical and magnetic field measurements, langmur probe, and mass flow controllers allowed continuous online computer control. The control system is based on multiphysics models using partial differential equations. This allows the etching to progress under optimal conditions for each layer.

11:40 AM Invited
Si Solar Cell Processing for Minimizing the Influence of Impurities and Defects: *Bhushan Sopori*[1]; [1]National Renewable Energy Laboratory, 1617 Cole Blvd., Golden, CO 80401 USA

Commercial silicon solar cells are fabricated on low-cost substrates that contain high concentrations of impurities and defects. To achieve high device efficiency, it is necessary to getter the impurities and to passivate the residual impurities and defects through hydrogenation. However, to maintain the cost-effectiveness, these processes must be included as a part of a typical cell fabrication sequence without increasing the number of process steps. This paper will review various approaches used to optimize impurity gettering and defect passivation in photovoltaic device fabrication. We will discuss the influence of each device process step on the changes in the impurity concentrations and the minority-carrier lifetime (or diffusion length), and discuss how defect passivation can be made a part of an efficient device fabrication schedule.

Modeling of High Temperature Alloy Processing - I

Sponsored by: Materials Processing & Manufacturing Division, Jt. Processing Modeling Analysis & Control Committee, Shaping and Forming Committee, Solidification Committee
Program Organizers: Matthew Krane, Purdue University, Department of Materials Engineering, West Lafayette, IN 47907 USA; Suhas P. Vaze, Concurrent Technologies Corporation, Johnstown, PA 15904 USA

Wednesday AM	Room: 310
February 20, 2002	Location: Washington State Conv. & Trade Center

Session Chairs: Suhas P. Vaze, Concurrent Technologies Corporation, 1450 Scalp Ave., Johnstown, PA 15904 USA; Matthew John M. Krane, Purdue University, Dept. of Matls. Eng., 1289 MSEE Bldg., W. Lafayette, IN 47907 USA

8:30 AM
The Use of 2D and 3D Finite Element Analysis to Simulate Evolution of Nickel Base Superalloy Billet Structure and Inspectability: *Bruce Fergus Antolovich*[1]; Bruce Andrew Lindsley[1]; Michael William Hill[1]; Howard William Sizek[2]; [1]Special Metals Corporation, 4317 Middle Settlement Rd., New Hartford, NY 13413 USA; [2]Special Metals Corporation, 100 Willowbrook Ave., Dunkirk, NY 14048 USA

Billets of nickel base superalloy intended for eventual use in rotating parts of modern turbine jets are subject to intense inspectability, grain size and mechanical property requirements. The conversion process from ingot structure to billet structure plays a crucial role in achieving these requirements. Cogging consists primarily of drawing operations in which the material is repeatedly deformed in a direction perpendicular to its longitudinal axis. Recent advances in numerical analysis capabilities have enabled the switch from 2 dimensional to 3 dimensional analyses for cogging. Direct prediction of grain size evolution during cogging is now possible and has been demonstrated. 3D finite element analysis has been used to better understand the role cogging plays in ultrasonic inspectability. Previous efforts in 2D have been very misleading due to previously unrecognized, but significant, interaction effects in the third dimension. Efforts using 3D modeling have allowed the better understanding of the development of billet structure and ultrasonic inspectability. This better understanding has in turn allowed for novel processing routes for improved structure and inspectability. The impact of forging route and use of 3D FEA upon ultrasonic inspectability of nickel base superalloy billets is discussed.

9:00 AM
Simulation of Directional Annealing: *I. Baker*[1]; J. Li[1]; A. Badmos[1]; H. J. Frost[1]; [1]Dartmouth College, Thayer Sch. of Eng., 8000 Cummings Hall, Hanover, NH 03755-8000 USA

A front-tracking, capillarity-driven, grain-growth model has been modified to simulate microstructural development during directional annealing. Preliminary simulations have been conducted for an infinite temperature gradient with a hot zone of uniform temperature moving along the length of the sample. The effects of the initial microstructure, hot zone velocity, hot zone width and grain boundary mobility have been investigated. A columnar grain structure is shown to form more easily with a finer initial grain structure and within a certain hot zone velocity range which depends on the grain boundary mobility, i.e. the hot zone peak temperature. The width of the hot zone is also shown to be critical in the development and continued propagation of a columnar grain structure. The effects of changing the temperature gradient ahead of the hot zone have also been investigated. Research supported by AFOSR grant F49620-00-1-0076 and NSF grant DMI9976509.

9:30 AM
A Software Tool to Design Preform and Die Shapes for Radial-Axial Profile Ring Rolling: *Anil Chaudhury*[2]; Chandrasekhar Reddy[1]; Urban De Souza[1]; Suhas Vaze[1]; Ken Phillips[3]; [1]Concurrent Technologies Corporation; [2]Applied Optimization, Fairborn, OH USA; [3]Firth-Rixson Viking, Reno, NV USA

On a radial-axial ring rolling mill, typical profile rings may be produced from a starting ring preform by using up to three mandrels and two king rolls. The design of dies and preforms has mostly relied on shop-floor experience and multiple "cut-and-try" methods. The process risks are high. For example, a ring part with the required profile but wrong diameter is considered 100% scrap and cannot be salvaged. Under these circumstances, computer simulation and design tools, which reduce process risk, offer tremendous potential to address cost reduction and process improvement for aerospace ring forged parts. Recently MSC.Software modified their 3D-finite element tool (MSC.MARC) to efficiently simulate the complex interaction between the rolls and the ring. To rapidly generate and evaluate preform and die shapes for the detailed analysis in MSC.MARC, a design tool (preForma-ring) was developed which will be described in this paper. This tool is capable of generating smooth intermediate shapes between preform and final part geometry in matter of minutes. These shapes are then evaluated using a number of geometric rules, which help to select the optimal preform shape for subsequent FEA evaluation and/or shop trials.

10:00 AM
Application of the Upper Bound Elemental Technique (UBET) to the Simulation of Profile Ring Rolling of High Temperature Alloys: *Jay Gunasekera*[2]; Vipul Ranatunga[2]; Urban De Souza[1]; Suhas Vaze[1]; [1]Concurrent Technologies Corporation, Johnstown, PA 15904 USA; [2]Ohio University, Dept. of Mechl. Eng., OH USA

Currently, simulation of profile ring rolling requires application of time-consuming 3-D finite element techniques. There is a need for rapid software tools to aid designers in developing ring-rolling process schedules thereby helping in reducing the design cycle time. The upper bound elemental technique is a rapid load estimating technique that has potential to meet this need and therefore its application to the unique 3-D flow situation experienced in profile ring rolling is being explored. This paper describes a UBET-based analytical method developed for the modeling of profile ring rolling of high temperature aerospace materials. The plastic flow of the material during rolling is described by dividing the deformation region between the two rolls (bite section) into rectangular and triangular prismatic elements and deriving kinematically admissible velocity fields for the 3-D material flow in each element. The currently developed method is capable of predicting ring diameter growth, die loads, material flow, ring strains and temperatures as a function of time. Numerical results have been compared with data available for high temperature alloys such as IN718 and Ti-6Al-4V.

10:30 AM Cancelled
Process Modeling of Thixotropic Forming Process of Steel Alloys: *Dierk C. Hartmann*

Modeling of Multi-Scale Phenomena in Materials Processing: Grain Boundary Phenomena

Sponsored by: ASM International: Materials Science Critical Technology Sector, Materials Processing & Manufacturing Division, Jt. Computational Materials Science & Engineering, Solidification Committee

Program Organizers: Adrian Sabau, Oak Ridge National Laboratory, MS-602, Oak Ridge, TN 37831-6083 USA; Boyd A. Mueller, Howmet Corporation, Whitehall, MI 49461-1832 USA; Anthony D. Rollett, Carnegie Mellon University, Department of Materials Science & Engineering, Pittsburgh, PA 15213-2890 USA

Wednesday AM	Room: 304
February 20, 2002	Location: Washington State Conv. & Trade Center

Session Chair: Anthony D. Rollett, Carnegie Mellon University, Matls. Sci. & Eng., Wean Hall 3327, 5000 Forbes Ave., Pittsburgh, PA 15213-2890 USA

8:30 AM
Providing a Length Scale by Capturing the Influence of Grain Boundaries in Polycrystal Plasticity Modeling: *Thomas E. Buchheit*[1]; Corbett C. Battaile[2]; Gerald W. Wellman[3]; Elizabeth A. Holm[2]; [1]Sandia National Laboratories, Dept. 1835, MS 0889, PO Box 5800, Albuquerque, NM 87185 USA; [2]Sandia National Laboratories, Dept. 1834, MS 1411, PO Box 5800, Albuquerque, NM 87185 USA; [3]Sandia National Laboratories, Dept. 9123, MS 0847, PO Box 5800, Albuqueque, NM 87185 USA

A material model which uses a crystal plasticity framework to simulate deformation response of polycrystalline metals has been implemented into JAS-3D, a quasistatic finite element code developed at SNL. The resultant microstructure-based deformation model has successfully performed 3-D simulations of realistic polycrystalline microstructures composed of 200 grains with approximately 200 elements per grain. Within this framework, a phenomenology has been devised that contains a gradient in hardening near grain boundaries. Simulations which include this phenomenology accurately capture the Hall-Petch effect and provide a length scale within the polycrystalline material response. Results will be presented. In addition, model results contain crystal orientation and hardening state variable information within each finite element of the model which can be compared with experimental data obtained by methods such as EBSD and nanoindentation. These type of microstructure level comparisons, useful in guiding development of this deterministic modeling approach, will also be included in the presentation. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin company, for the United States Department of Energy under Contract DE-AC04-94AL85000.

8:55 AM
Simulation Studies of Grain Boundary Diffusion in NiAl: *Diana Farkas*[1]; Benjamin Soule de Bas[1]; [1]Virginia Tech, Dept. of Matls. Sci., Blacksburg, VA 24060 USA

We present the results of large scale molecular dynamics simulations of grain boundary diffusion in B2 NiAl. The studies use EAM interatomic potentials to simulate the diffusion process in a direct manner, starting with vacancies located in different sites in the grain boundary region. The simulations show a variety of diffusion jumps, all introducing disorder in the grain boundary. This is in contrast to diffusion in bulk NiAl, where cyclic mechanisms, restore order. Several series of correlated jumps were identified in the grain boundary region. The most common of these result in the vacancy remaining in the same structural unit. The mechanisms of the vacancy diffusing to a neighboring structural unit were also observed and are reported in detail.

9:20 AM
Subgrains Formation in Uranium as an Experimental Tool for Dislocation Plasticity: *Gabriel Abraham Frank*[1]; Roni Zvi Shneck[1]; Alex Landau[2]; Arie Venkert[2]; [1]Ben-Gurion University of the Negev, Dept. of Matls. Eng., PO Box 653, Beer Sheva 84105 Israel; [2]NRCN, PO Box 9001, Beer Sheva Israel

Texture formation and dislocation patterning into walls and cells are long-standing questions in the theory of plasticity that may benefit from the study of the deformation of metals having low symmetry. A central difficulty in analysis of the deformation of most metals is the multiplicity of slip systems, which gives rise to ambiguities in the selection of the active systems. We study the subgrain formation in uranium during β-α phase transformation and illustrate its association with predictable plastic deformation. These subgrains were suggested to be creep cells formed by the plastic deformation accommodating the transformation strains. The low ambiguity allows determining a unique combination of the active slip systems. Misorientations across subgrains in α-uranium were determined by SAD/TEM and shown to be accommodated by the dislocations arising from the active slip systems. Frank-Bilby equation was used to determine the relative densities of the dislocations in each boundary.

9:45 AM Break

10:00 AM
Experimental Characterization of the Three-Dimensional Dislocation Substructure Evolution in Copper during Changing Strain Paths for Input and Validation of the Dislocation Dynamics Models: *Rodney J. McCabe*[1]; Amit Misra[1]; Terence E. Mitchell[1]; Michael G. Stout[1]; George C. Kaschner[1]; Kathleen B. Alexander[1]; [1]Los Alamos National Laboratory, MST-8 Struct./Prop. Relations Grp., MS-G755, Los Alamos, NM 87545 USA

Innovative modeling techniques are being developed at all length scales that incorporate three-dimensionality of the relevant microstructures. However, the body of experimental work available for 3D model input and validation is limited. We have performed a detailed, quantitative TEM study of the 3D dislocation substructure evolution in polycrystalline copper loaded monotonically as well as under changing strain paths. Stereo-TEM is used to reveal the three-dimensional dislocation configurations that can be used as input for dislocation dynamics models or as verification of the predicted equilibrium dislocation structures. In situ straining TEM, in conjunction with post mortem TEM, are useful for tracking the evolution of individual dislocations and dislocation substructures. Through this quantitative TEM study, we interpret the macroscopic work hardening/softening observed under changing strain paths and provide experimental support for the 3D dislocation dynamics simulations. This research is funded by the US Department of Energy, Office of Basic Energy Sciences.

10:25 AM
Investigation of Temperature Influence on Film Structure using the Level Set Method: *Anthony Tongen*[1]; David L. Chopp[1]; [1]Northwestern University, Eng. Scis. & Appl. Math., 2145 Sheridan Rd., Evanston, IL 60208 USA

We investigate two dimensional grain growth by means of the level set method. This study examines the relationship between film growth temperatures and the preferred orientation of surface crystals. Some materials, such as TiN, can have disparate textures due to different annealing temperatures. For instance, at 800° the (001) orientation is observed, while at room temperature the (111) face dominates. The predominant orientation of the film controls the material properties of the overall film. The level set method is a powerful method for moving fronts which can handle sharp corners and cusps in the interface and topological changes naturally. Anisotropic surface diffusion, a fourth order nonlinear operator, is often the rate limiting step in numerical simulations. We have employed a new technique coupling the level set method with a marker particle method to speed up the computational time. We simulate deposition and annealing to demonstrate agreement with experimental results.

10:50 AM
The Impact of Anisotropic Grain Boundary Properties on Texture Development: *Anthony D. Rollett*[1]; [1]Carnegie Mellon University, Dept. of Matls. Sci. & Eng., Wean Hall 4315, 5000 Forbes Ave., Pittsburgh, PA 15213 USA

Since grain boundary properties are generally highly anisotropic, their impact on other material properties is of great interest. For example, the strong variation in grain boundary mobility observed for the transition from low angle to high angle boundaries can lead to highly abnormal grain growth. This effect of grain boundary properties has been explored computationally with a Monte Carlo model that incorporates texture. When coarsening (grain growth) is simulated in a single crystal that possesses a finite (mosaic) spread in orientation, abnormal grain growth occurs for a particular critical dispersion. This behavior represents one mechanism for the appearance of recrystallization nuclei. The grain boundary properties used in the simulations represent a distillation of experimental and theoretical information. The latter have largely been obtained through Monte Carlo and molecular dynamics simulations of the structure and kinetics of boundaries. As an example of their importance, the growth of the {001}<100> component in fcc metals has been found to be highly dependent on the grain boundary properties.

11:15 AM
Process Design to Achieve Targetted Microstructures: The Spectral Method: *Surya R. Kalidindi*[1]; Joshua Houskamp[1]; Brent L. Adams[2]; Hamid Garmestani[3]; [1]Drexel University, Matls. Eng., Philadelphia, PA 19104 USA; [2]Brigham Young University, 435 CTB, Provo, UT 84602 USA; [3]FAMU-FSU College of Engineering, Tallahassee, FL 32310 USA

The authors have recently developed and reported a new paradigm to facilitate materials by design by using spectral representations of microstructure and the associated properties. In an accompanying paper, the tremendous advantages of using the spectral method in describing the universe of all relevant microstructures for the design problem at hand (denoted as the material hull) and the space of all physically realizable property combinations (denoted as the property closure) are being described in detail. In this paper, this paradigm will be extended to include considerations of process design that is predicted to result in pre-selected microstructures. It will be shown that there are significant advantages to describing microstructure evolution in the Fourier space. Specifically, the concept of streamlines has been used to mathematically represent both the microstructure evolution in the material hull and the concomitant property evolution in the property closure. The newly developed methodologies will be demonstrated in the context of the design example.

11:40 AM
Incorporation of Deformation Twinning in Modeling the Mechanical Behavior of A-Titanium: *Ayman A. Salem*[1]; Surya R. Kalidindi[1]; Roger D. Doherty[1]; [1]Drexel University, Dept. of Matls. Eng., Philadelphia, PA 19104 USA

In this work we have modeled the stress-strain response and the texture evolution of a-Titanium using a polycrystal plasticity model. The model incorporated both crystallographic slip and deformation twinning as the modes of plastic deformation. The validity of the model was verified through comparisons of predicted textures and stress-strain curves with the direct measurements. The experiments included simple compression, plane strain compression, and simple shear tests. Texture measurement and twin volume fraction were evaluated by orientation imaging microscopy. Deformation twinning was found to play a vital role in the strain hardening behavior of a-Titanium. The onset of deformation twinning was associated with a marked increase in the strain hardening rate. Deformation twins are believed to reduce the effective slip distance and increase the strain hardening rate via Hall-Petch hardening mechanism. When slip, as a competing deformation mechanism, became dominant, the effect of twinning on strain hardening rate was found to saturate.

Phase Stability, Phase Transformations & Reactive Phase Formation in Electronic Materials - II

Sponsored by: Electronic, Magnetic & Photonic Materials Division, Structural Materials Division, Alloy Phases Committee
Program Organizers: Sinn-Wen Chen, National Tsing-Hua University, Department of Chemical Engineering, Hsinchu City 300 Taiwan; C. Robert Kao, National Central University, Department of Chemical Engineering, Chungli City, Taiwan; Hyuck Mo Lee, Korea Advanced Institute of Science & Technology, Department of Materials Science & Engineering, Taejon 305-701 Korea; Michael R. Notis, Lehigh University, Department of Materials Science, Bethlehem, PA 18015 USA; Douglas J. Swenson, Michigan Technological University, Department of Metallurgical & Materials Engineering, Houghton, MI 49931 USA

Wednesday AM — Room: 211
February 20, 2002 — Location: Washington State Conv. & Trade Center

Session Chairs: H. M. Lee, Korea Advanced Institute of Science and Technology, Dept. of Matls. Sci. & Eng., Kusung-Dong 373-1, Yusung-Gu, Taejon 305-701 Korea; S. W. Chen, National Tsing-Hua University, Dept. of Chem. Eng., #101 Kuang-Fu Rd., Sec. 2, Hsin-Chu 30043 Taiwan

8:30 AM Invited
The Constitution of the In2O3-SnO2 System: Implications for Transparent Conducting Oxide Applications: *Douglas J. Swenson*[1]; William J. Heward[1]; [1]Michigan Tech University, Matl. Sci. & Eng., 1400 Townsend Dr., Houghton, MI 49931 USA

SnO2-doped In2O3, also referred to as indium-tin-oxide or ITO, is a leading commercial transparent conducting material. Although widely utilized in commercial products, basic information available about the phase stability of ITO is lacking, a situation that hampers effective optimization of its processing-properties-structure relationships. In this work, phase equilibria in the In2O3-SnO2 system have been studied over the entire composition range between 1000 and 1650°C, using electron probe microanalysis and x-ray diffraction analysis. Two ternary phases, In4Sn3O12 and In2SnO5, were found to exist in this system. Both phases are stable only at high temperatures, decomposing eutectoidally at 1325 and 1600°C, respectively. The maximum solubility of SnO2 in In2O3 was found to increase dramatically with increasing temperature, ranging from 1.3 mol% at 1000°C to 13.1 mol.% at 1650°C. These results suggest that most commercially produced ITO thin films are thermodynamically metastable, being substantially supersaturated with SnO2. Other implications of the study are also discussed.

8:55 AM

Preferential Dissolution and Inter-Metallic Compound Formation with Multi-Component Base Metal and Solder Alloys: *Kenneth L. Erickson*[1]; Polly L. Hopkins[1]; Paul F. Hlava[1]; Paul T. Vianco[1]; Jerome A. Rejent[1]; [1]Sandia National Laboratories, PO Box 5800, Albuquerque, NM 87185 USA

An understanding of the physical and chemical mechanisms controlling reaction between base metal and molten solder is important for developing soldering processes, particularly for multi-component base metal and solder alloys. Depending on materials and process conditions, solid-solid and liquid-solid reactions coupled with solid-state and liquid-phase diffusion can cause preferential dissolution of base metal constituents and non-equilibrium inter-metallic compound formation between base metal and solder. For example, recent experiments with 76Au-21Pt-3Pd (wt%) alloy sheet and 63Sn-37Pb solder showed that preferential dissolution of Au by molten 63Sn-37Pb solder causes formation of Pt-rich inter-metallic compounds between alloy sheet and molten solder. During subsequent solid-state aging the Pt-rich compounds transform to Au-rich inter-metallic compounds consistent with the initial base metal composition. This paper summarizes results from experiments with 76Au-21Pt-3Pd (wt%) alloy sheet and 63Sn-37Pb solder and discusses the computational models developed to examine the competing effects of diffusion and reactive phase formation and dissolution.

9:15 AM Invited

Diffusion and Interfacial Reactions between Thin-Film Ti/Ni/Ag Metallization and a Lead-Free Solder: *Gautam Ghosh*[1]; [1]Northwestern University, Dept. of Matls. Sci. & Eng., 2225 N. Campus Dr., Evanston, IL 60208-3108 USA

The interfacial reactions involving thin-film Ti/Ni/Ag metallizations on two semiconductor devices, diode and MOSFET, a Sn-3Ag-0.7Cu solder, and a Au-layer on the substrate are studied. Interfacial reactions are investigated during reflow process and during accelerated aging at 125°C. To understand the interdiffusion processes, the interfacial reaction products are characterized using SEM, TEM and AEM. Two intermetallics, Ni_3Sn_4 and Cu_6Sn_5, are found to form during reflow process. The primary microstructural dynamics during solid state aging are the coarsening of intermetallic particles and reactions involving the Ni- and Ti-layer with Au and Sn. While the reaction with the Ni-layer yields only Ni_3Sn_4, reaction involving the Ti-layer suggests the formation of Ti-Sn and Au-Sn-Ti intermetallics. These results along with the relevant phase stability and the diffusion mechanism will be discussed in detail.

9:40 AM Invited

Flux-Free Direct Chip Attachment of Flip Chip with Lead-Free Solder Bump: *Choon-Sik Kang*[1]; Soon-Min Hong[1]; Jae-Pil Jung[2]; [1]Seoul National University, Sch. of Matls. Sci. & Eng., San 56-1, Shillim-dong, Kwanak-ku, ENG445_F, Seoul 151-744 Korea; [2]University of Seoul, Dept. of Matls. Sci. & Eng., 90 Jeonnong-dong, Dongdaemun-ku, Seoul 130-743 Korea

The flux in soldering removes contaminants and dissolves surface oxides to improve solderability. The application of flux, however, could lead to the corrosion of the circuit and deterioration of long-time reliability due to the flux residues in the joint. Especially in fine pitch flip chip package, the residual flux may exist in the region where removal of the residue is almost impossible. Besides, using flux causes environmental concerns, so manufacturer needs to find an effective replacement of the flux. Therefore, fluxless soldering is becoming an active research area. In this work, fluxless bonding of flip chip with Sn-Pb and Sn-Ag solder bump to Glass substrate was studied with the purpose of optoelectronics application. Instead of flux, plasma treatment was used to remove the oxides and other contaminants. The degree of oxide removal on solder surface was examined by AES. The effect of flip chip process parameters were evaluated and discussed.

10:05 AM Break

10:25 AM Invited

Reliability Issues of Pb-Free Soldering Caused by Metallurgical Reactions: *Kejun Zeng*[1]; King-Ning Tu[1]; [1]UCLA, Dept. of Matls. Sci. & Eng., 6532 Boelter Hall, Los Angeles, CA 90095-1595 USA

Some reliability issues of Pb-free solder processing in electronic packaging technology, that are caused by metallurgical reactions between solder and under-bump-metallizations (UBM), are discussed. These include the formation of the interfacial intermetallic compounds, interfacial segregation, contamination of Pb-free solder joints, and compatibility of UBM and surface finishing with Pb-free solders. Thermodynamic calculations and kinetic considerations are applied to the above cases. Attention has been paid to the influences of processing or experimental conditions on the microstructural stability of the interfacial areas in solder joints and the joint reliability.

10:50 AM Invited

Solder Joint Strength and Interfacial Reaction between Cu/X (X=Ni, Ag or Ni/Ag) Substrate and Sn-36Pb-2Ag Solder Alloy: Seung Wook Yoon[1]; *Jong Hoon Kim*[2]; Chang Joon Yang[2]; Hyuck Mo Lee[2]; [1]Hynix Semiconductor Corporation, Pkg./Module R&D, San 136-1, Ami-ri, Bubal-eub, Ichon-si, Ichon, Kyoungki-do 467-701 Korea; [2]Korea Advanced Institute of Science and Technology, Dept. of Matls. Sci. & Eng., Kusung-Dong 373-1, Yusung-Gu, Taejon 305-701 Korea

Interfacial reaction between electroplated Ni, Ag or Ag/Ni on Cu alloy substrate and Sn-36Pb-2Ag solder ball was investigated and their bonding strengths were measured with Dage2000 ball shear tester. Ag3Sn IMC was found at the interface between 2mm-Ag/solder ball and Ni3Sn4 was for 2mm-Ni/solder ball. In case of 2mm-Ag/2mm-Ni electroplated Cu substrate, there were Cu/Ni/Ni3Sn4/Ag3Sn/solder layers formed at interface and each IMCs were confirmed by EDX analysis. Ag layer was completely consumed by formation of Ag3Sn, but most Ni layer was remained. After various environmental tests, Ag/Ni plated Cu substrate had superior solder joint reliability than other Ni or Ag single plated Cu substrate. Two different type of reflow profile were investigated and the specimens prepared by higher soldering temperature showed superior solder joint strength. The solder joint strength and the microstructural change were observed with number of reflow cycle in considering the real board mounting. There was drastical evolution of microstructure and these could explain the solder joint strength change with reflow cycles.

11:15 AM Invited

Interface Reactions between 50In-50Pb and Copper Substrates Due to Solid-State, Acclerated Aging: *Paul Thomas Vianco*[1]; Jerome Rejent[1]; Alice Kilgo[1]; Paul Hlava[1]; [1]Sandia National Laboratories, Dept. 1835, PO Box 5800, MS 1411, Albuquerque, NM 87185-1411 USA

A study examined the interface reaction between 50In-50Pb (wt.%) solder and Cu substrates. Substrates were hot dipped in the molten In-Pb solder and aged at 55, 70, 100, 135, and 170°C for time periods of 1 to 350 days. The reaction layer composition was determined by electron microprobe analysis. The growth kinetics were calculated from layer thickness data. Ring-and-plug shear test samples were fabricated and aged for 10, 50, and 100 days under 55, 100, and 170°C. Aging caused as strength increase for a gap of 0.008 in; however, the strength decreased with aging when the gap was enlarged to 0.015 in. The fracture morphology as well as the impact of the reaction layer on shear strength will be discussed. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the US Dept. of Energy under contract DE-AC04-94AL85000.

Processing and Properties of Lightweight Cellular Metals and Structures
The MPMD Third Global Symposium
Processing and Service Properties - Session V

Sponsored by: Materials Processing & Manufacturing Division, Jt. Computational Materials Science & Engineering, Powder Materials Committee, Jt. Processing Modeling Analysis & Control Committee, Surface Engineering Committee, Shaping and Forming Committee, Solidification Committee

Program Organizers: Amit K. Ghosh, University of Michigan, Department of Materials Science and Engineering, Ann Arbor, MI 48109-2136 USA; T. Dennis Claar, Fraunhofer USA, Newark, DE 19716 USA; T. H. Sanders, Georgia Institute of Technology, Department of Materials Science and Engineering, Atlanta, GA 30332 USA

Wednesday AM — Room: 205
February 20, 2002 — Location: Washington State Conv. & Trade Center

Session Chairs: Tom H. Sanders, Georgia Institute of Technology, Dept. of Matls. Sci. & Eng., Atlanta, GA 30332 USA; T. Dennis Claar, Fraunhofer USA, 501 Wyoming Rd., Newark, DE 19716 USA

8:30 AM
Compressive Properties of Maraging Steel Honeycomb under Quasi-Static and Dynamic Loading: *Alethea M. Hayes*[1]; David L. McDowell[2]; Joe K. Cochran[1]; [1]Georgia Institute of Technology, Matls. Sci. & Eng., 771 Ferst Dr., Atlanta, GA 30332-0245 USA; [2]Georgia Institute of Technology, Mech. Eng., 801 Ferst Dr. N.W., Atlanta, GA 30332-0405 USA

Two-dimensional linear cellular solids or honeycombs are known for their high-strength to weight ratios compared to other low-density architectures. Georgia Tech has developed a process that produces honeycomb from maraging steel compositions including the 18% Ni series, which has high yield and ultimate strength after heat treatment. This steel incorporated into a honeycomb structure with a relative density of 20-25% produced very high compressive strength under both quasi-static and dynamic loading conditions. Both quasi-static and dynamic experiments were conducted for the out-of-plane direction of the maraging steel honeycombs. The dynamic data was generated by the split Hopkinson pressure bar and produced strain-rates on the order of 103 sec-1. Peak compressive strengths, collapse modes, and strain-rate sensitivity were examined in this study. The experimental peak quasi-static results were compared to the models developed by Thomas Wierzbicki and Lorna Gibson and Michael Ashby. All of the models under-predicted the collapse strength for this material, despite the presence of honeycomb defects and cell wall porosity inherent in this developing process. In addition, the strain-rate sensitivity for the maraging steel was very minimal.

8:55 AM
Processing and Properties of Steel Foam Materials and Structures: *T. Dennis Claar*[1]; Virgil Irick[1]; Kenneth Kremer[1]; Jim Adkins[1]; [1]Fraunhofer USA, Ctr. for Mfg. & Adv. Matls., 501 Wyoming Rd., Newark, DE 19716 USA

The powder metallurgy-based foaming process is capable of producing foams from a variety of metals, including aluminum, tin, lead, copper, and iron. This paper will focus on the processing and properties of steel foams for weight reduction of engineering structures. Steel foam precursors are produced by mixing iron powders with alloying elements and a foaming agent, and then consolidating the powder mixtures into dense compacts via hot isostatic pressing, hot pressing, extrusion, or hot rolling processes. The precursor material is then foamed by heating into the semi-solid state, during which evolved gas forms the closed-cell foam structure. The effects of precursor consolidation method, as well as various alloy and foaming agent additions, on steel foam microstructure will be discussed. The relationship between steel foam compressive strength and porosity level will be shown and compared with aluminum and titanium metal foams. The fabrication and characterization of steel foam sandwich panels and foam-filled tubes will be described. Potential uses of steel foams in ship structures, automotive, and other applications will be presented.

9:20 AM
Fabrication and Creep Studies on Open Cell Nickel Structures: *R. K. Oruganti*[1]; A. K. Ghosh[1]; [1]University of Michigan, Matls. Sci. & Eng., 2300 Hayward, Ann Arbor, MI 48109 USA

Open cell Ni-base alloy porous structures have potential for light-to-medium load bearing applications at elevated temperatures while they may also be actively cooled by fluid flow. In this study, fabrication of open-cell Ni structures was made by using two different processes. A process to create honeycomb cells was developed that relied on diffusion bonding of thin-walled tubes wherein sintering forces were used to convert circular core wall geometry into hexagonal ones. Linear cellular structures with very low density (6% dense) were prepared by this method. The other process utilized woven wire mat to diffusion bond a layered stack to create denser structure (56% dense). Compressive creep behavior of these structures was characterized as a function of the cell size and orientation and the results compared with those of a solid material. Inhomogeneity of deformation and large springback response differentiate the creep behavior of such cellular structures from that of solid materials. Among other features, a thermoelastic after-effect in cooling from test temperature and a mode of shear instability in progressive collapse of the cells during large deformation are seen.

9:45 AM Break

10:05 AM Cancelled
The Stiffness and Weldability of an Ultra-Light Steel Sandwich Sheet Material with a Fibrous Metal Core: *Bill Clyne*

10:05 AM
Fabrication, Mechanical Properties, and In-Situ Diffraction Strain Measurements in Aluminum-Mullite Microsphere Syntactic Foams: *Dorian K. Balch*[1]; David C. Dunand[1]; [1]Northwestern University, Dept. of Matls. Sci. & Eng., MLSB 2036, 2225 N. Campus Dr., Evanston, IL 60208-3108 USA

High-strength aluminum syntactic foams are fabricated using a liquid metal infiltration technique. Unalloyed and 7075 aluminum are infiltrated into a packed bed of hollow ceramic spheres. The spheres consist of a combination of crystalline mullite (3 Al2O3-2 SiO2) and amorphous silica (SiO2), and have diameters of 15-75 microns and wall thicknesses of 5-10 microns. Melting of the aluminum under vacuum followed by pressurization of the infiltrator with inert gas to 3.5 MPa forces the liquid metal between the packed spheres, producing foams with relative densities between 0.45 and 0.60 (1.3-1.6 g/cm3). High compressive strengths have been observed, 100-250 MPa depending on alloy and heat treatment, with high densification strains and exceptional energy absorption. In-situ measurements of lattice strains within the mullite phase during compressive loading are performed using high-energy synchrotron x-rays, permitting investigation of sphere stresses and foam damage evolution during loading.

10:30 AM
Vibration Properties of Closed-Cell Aluminum Foam: H. F. von Bremen[1]; V. S. Sokolinsky[1]; S. Rajaram[1]; H. Shen[1]; Z. Song[1]; Y. Zhou[1]; *Steven R. Nutt*[1]; [1]University of Southern California, Matls. Sci., 3651 Watt Way, VHE-602, Los Angeles, CA 90089-0241 USA

Aluminum foam may be useful as a core for sandwich structures. Many applications of sandwich structures experience dynamic excitations. Therefore, it is important to assess the vibration properties of aluminum foam. A simple experimental layout consisting of a shaker and an accelerometer is used to investigate the natural vibration modes of a cantilever aluminum foam beam. The natural vibration frequencies of the beam were measured over 20-5000 Hz. The experimentally established natural frequencies are compared with theoretical predictions. The results of experimental and theoretical studies are discussed and conclusions are drawn. Experiments show that damping properties of the foam core are manifest most noticeably in the case of symmetric vibration modes, whereas the influence on anti-symmetric modes is insignificant. The experimental measurements are in good agreement with the analytical predictions of the higher-order sandwich theory. Supported by Honda R&D Americas.

10:55 AM
Development of Vibration Damping Techniques in Metallic-Intermetallic Laminate (MIL) Composites: *Aashish Rohatgi*[1]; Kenneth S. Vecchio[1]; John B. Kosmatka[2]; [1]University of California, Mech. & Aeros. Eng., 9500 Gilman Dr., EBU-2, Rm. #262, La Jolla, CA 92093-0411 USA; [2]University of California, Struct. Eng., 9500 Gilman Dr., La Jolla, CA 92093-0085 USA

Lightweight Ti-Al3Ti metal-intermetallic laminate (MIL) composites with Lodengraf damping have been developed. Lodengraf damping was achieved by creating cylindrical cavities in the composites and filling them with low density glass spheres. For a given Ti-Al3Ti composition, the damping characteristics of the MIL composites was controlled by varying the location and size of the cavities, and by varying the size and quantity of glass spheres used to fill these cavities.

These "porous" MIL composite plates were vibration tested using an acoustic excitation and a non-contacting scanning laser vibrometer to determine their modal properties (natural frequency, mode shapes and damping properties). An extra layer of ferritic stainless steel was incorporated in several "porous" Ti-Al3Ti composites. Vibration induced stress oscillations may produce eddy current damping in such composites, in addition to the Lodengraf damping. The dependence of damping on the processing variables i.e. the size and distribution of perforations, and the size and amount of glass beads, will be highlighted. The effect of introducing porosity on the mechanical strength and toughness will also be described.

Second International Symposium on Ultrafine Grained Materials: Superplasticity and Thermal Stability

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

Program Organizers: Yuntian Ted Zhu, Los Alamos National Laboratory, Materials Science and Technology Division, Los Alamos, NM 87545 USA; Terence G. Langdon, University of Southern California, Department of Mechanical Engineering, Los Angeles, CA 90089-1453 USA; Terry C. Lowe, Technanogy, Newport Beach, CA 92627 USA; Rajiv S. Mishra, University of Missouri, Metallurgical Engineering, Rolla, MO 65409-0340 USA; Michael Jeremi Saran, Case Western Reserve University, Cleveland, OH 44106 USA; S. Lee Semiatin, Air Force Research Laboratory, Materials & Manufacturing Directorate, WPAFB, OH 45433 USA

Wednesday AM — Room: 210
February 20, 2002 — Location: Washington State Conv. & Trade Center

Session Chairs: Terence G. Langdon, University of Southern California, Depts. of Aeros. & Mechl. Eng. & Matls. Sci., Los Angeles, CA 90089 USA; Zenji Horita, Kyushu University, Dept. of Matls. Sci. & Eng., Fac. of Eng., Fukuoka 812-8581 Japan

8:30 AM Keynote
Superplasticity in Ultrafine Grain Materials: *Amiya K. Mukherjee*[1]; [1]University of California, Chem. Eng. & Matls. Sci., One Shields Ave., Davis, CA 95616 USA

One of the most important requirements for superplasticity is the presence of fine grain size having high angle boundaries that slide easily. Recent advances in materials processing have now produced new avenues for grain size refinement. Some of these avenues for producing ultrafine grain materials (including the process of high pressure torsion) will be described. Superplasticity has been revealed in ultrafine grain (including nano-sized grain) microstructure. The prediction of both high strain rate superplasticity and low temperature superplasticity have materialized. However, the flow stresses and strain-hardening rates for superplasticity in nanocrystalline materials are much higher than that in microcrystalline materials. The reason for this observation is not entirely clear at present. This research is supported by NSF-DMR-9903321.

8:55 AM
Developing Superplasticity at High Strain Rates through ECAP Processing: *Terence G. Langdon*[1]; Minoru Furukawa[2]; Zenji Horita[3]; [1]University of Southern California, Dept. of Aeros. & Mech. Eng. & Matls. Sci., Los Angeles, CA 90089-1453 USA; [2]Fukuoka University of Education, Dept. of Tech., Munakata, Fukuoka 811-4192 Japan; [3]Kyushu University, Dept. of Matls. Sci. & Eng., Fac. of Eng., Fukuoka 912-8581 Japan

Processing by equal-channel angular pressing (ECAP) leads to exceptional grain refinement, typically to the submicrometer or nanometer level, and thus to an opportunity to attain superplastic ductilities at very rapid strain rates. This paper describes the specific requirements in order to achieve high strain rate superplasticity in as-processed materials and examples are given to demonstrate the feasibility of this processing method.

9:10 AM
Microstructural Evolution on Annealing of a Severely Deformed Al 3%Mg Alloy: *Jody Scott Hayes*[1]; P. B. Prangnell[1]; P. Bate[1]; [1]UMIST, Matls. Sci. Ctr., Grosvenor St., Manchester M1 7HS UK

An Al 3%Mg alloy has been severely deformed by the ECAE process. Billets of the alloy have been subjected to multiple passes to achieve an effective strain of 10. The severely deformed microstructure was subsequently annealed at a range of temperatures. Recrystallisation and grain growth behaviour was studied. The as-processed and low temperature anneal samples have been studied using the TEM. By measuring grain widths, lengths and misorientations, the evolution of a fine equiaxed structure from a very long thin deformation structure has been investigated. Subsequent grain growth in higher temperature anneals have been studied in the FEGSEM using EBSD analysis. Using data from the TEM and FEGSEM, the annealing behaviour was modelled using Monte Carlo-Potts and Network simulations. These showed a very rapid initial change from a high aspect ratio to equiaxed grains followed by essentially normal grain growth, though the effects of boundary misorientation needs to be considered.

9:25 AM
Enhanced Formability of Superplastic AlMgZr Alloys made by Particulate Routes: *Ray Cook*[1]; Roger Grimes[2]; Richard Dashwood[2]; [1]The Aluminium Powder Company, Ltd., Forge Ln., Minworth, Sutton Coldfield, W. Midlands B76 1AH UK; [2]Imperial College of Science Technology and Medicine, Dept. of Matls., Exhibition Rd., London SW7 2AZ UK

The technique of centrifugal atomisation has been used to produce a number of AlMgZr alloy particulates with Zr contents up to 1% that have been converted into sheet by extrusion, rolling and heat treatment and their superplastic properties determined. It has been found that control of the solidification conditions during atomisation is crucial in order to maximise Zr solid solubility and achieve a fine dispersion of Al_3Zr precipitates. Superplastic behaviour is enhanced at higher Zr contents, and by thermo-mechanical processing to achieve ductilities in excess of 600% at strain rates of 0.01 s^{-1}. Alloy conditioning was found to have a significant effect on the Al_3Zr precipitate size, with coarser precipitates relating to premature failure during testing. This paper describes the atomisation process and identifies the key parameters that must be controlled for its successful operation. A summary of the superplastic performance of the product will be included.

9:40 AM Invited
Grain Refinement and Superplasticity in Magnesium Alloys: *Hiroyuki Watanabe*[1]; Toshiji Mukai[1]; Kenji Higashi[2]; [1]Osaka Municipal Technical Research Institute, Mech. Eng. Dept., 1-6-50 Morinomiya, Joto-ku, Osaka 536-8553 Japan; [2]Osaka Prefecture University, Dept. of Metal. & Matls. Sci., 1-1 Gakuen-cho, Sakai, Osaka 599-8531 Japan

Intriguing superplastic behavior, such as high-strain-rate superplasticity and/or low temperature superplasticity, can be attained when the materials are refined to extremely fine-grained conditions because of the significant grain size dependence of this phenomenon. In addition, effect of particle and grain boundary structure on superplastic flow, which is indispensable to understand the nature or limit of superplasticity, can be investigated using low-temperature superplastic materials. In the present study, fine-grained Mg-Zn-Zr alloys have been processed by powder metallurgy route or equal-channel-angular extrusion. The materials could be refined to a sub-microcrystalline structure through these two procedures. Superplastic behavior was examined for both materials at low temperatures of ~473 K in order to shed light on the mechanism of superplastic flow. Data analyses revealed some interesting features of superplasticity, which were not found until the grain sizes reduced to the order of sub-micron.

10:00 AM
Processing of an Aluminum-6061 Metal Matrix Composite by Equal-Channel Angular Pressing: *Yi Huang*[1]; Cheng Xu[1]; Sangmok Lee[1]; Minoru Furukawa[2]; Zenji Horita[3]; Terence G. Langdon[1]; [1]University of Southern California, Dept. of Aeros. & Mech. Eng. & Matls. Sci., Los Angeles, CA 90089-1453 USA; [2]Fukuoka University of Education, Dept. of Tech., Munakata, Fukuoka 811-4192 Japan; [3]Kyushu University, Dept. of Matls. Sci. & Eng., Fac. of Eng., Fukuoka 812-8581 Japan

An Al-6061 metal matrix composite, reinforced with 10 vol% Al_2O_3 particulates, was subjected to equal-channel angular (ECA) pressing. The grain size of the composite was reduced to the submicrometer level through processing by ECAP. The mechanical properties of the material were investigated using tensile tests at high temperatures over a range of strain rates. This paper describes and discusses the mechanical properties of the composite after ECAP and presents representative microstructures obtained using TEM.

10:15 AM Break

10:25 AM Keynote
Grain Refinement of Copper Based Alloys using ECAP: *Zenji Horita*[1]; Koji Neishi[1]; Terence G. Langdon[2]; [1]Kyushu University, Fac.

of Eng., Dept. of Matls. Sci. & Eng., Fukuoka 812-8581 Japan; [2]University of Southern California, Dept. of Aeros. & Mechl. Eng. & Matls. Sci., Los Angeles, CA 90089-1453 USA

Equal-channel angular pressing (ECAP) was conducted for grain refinement of Cu alloys containing Zn and/or Zr. The ECAP samples were subjected to static annealing at elevated temperatures. Microstructures were observed by transmission electron microscopy and tensile properties were examined at elevated temperatures. Microstructural features after static annealing were compared with those of Al alloys. It is shown that recrystallization occurs discontinuously in ECAP-Cu alloys whereas grains grow continuously in ECAP-Al alloys without having the nucleation of recrystallized grains. In ECAP-Cu alloys, the recrystallization temperature depends sensitively on the contents of Zn or Zr. It is also shown that superplasticity was attained at an optimized condition for an ECAP-Cu alloy.

10:50 AM

Structure, Properties and Thermal Stability of Ultra-Fine Grain Cu-Cr-Zr Bronze: *Alexei Vinogradov*[1]; Vsevolod Patlan[2]; Kazuo Kitagawa[2]; Vladimir I. Kopylov[3]; [1]Osaka City University, Dept. Intelligent Matls. Eng., Osaka 558-8585 Japan; [2]Kanazawa University, Mech. Sys. Eng., Kodatsuno 2-40-20, Kanazawa 920-8667 Japan; [3]Physical-Technical Institute of the National Academy of Science, Minsk 220730 Belarus

The structure, thermal stability, mechanical and electrical properties are investigated of ultra-fine grain Cu-Cr-Zr bronze obtained by equal-channel angular pressing (ECAP). Strengthening mechanisms resulting from a combination of intensive cold work and subsequent aging have been taken advantage of to produce materials which have good electrical conductivity, hardness, tensile strength and excellent thermal stability, have sufficient ductility for forming and also effectively resist fatigue stressing. Optimal post-processing aging conditions were found to ensure a desired combination of properties. A special attention is paid to the fatigue behavior, which is characterized in both strain, and load controlled experiments. Fatigue mechanisms and nature of cyclic softening is discussed. Experimental data unambiguously show that the Cu-Cr-Zr bronze processed in the ECAP-aging scheme has significant advantages over currently available, commercial tempers in that it permit designs having much higher working stresses and better material utilization, thus providing a better cost effectiveness.

11:05 AM

Effect of Thermal Stability of Microstructure on the Tensile Properties: *Bing Q. Han*[1]; Terence G. Langdon[2]; [1]University of California, Dept. of Chem. & Biochem. Eng. & Matls. Sci., Irvine, CA 92697-2575 USA; [2]University of Southern California, Depts. of Aeros. & Mechl. Eng. & Matls. Sci., Los Angeles, CA 90089-1453 USA

Severe plastic deformation of a commercial 2219 Al alloy was performed through equal-channel angular pressing at room temperature. Ultrafine grains of about 0.2 mym were present after 8 and 12 passes. However, superplasticity of ultrafine-grained Al 2219 alloy was not observed at temperatures from 573 to 673 K. Although there are precipitates of q¢ or q in the microstructure of the Al 2219 alloy, they are not sufficiently strong to inhibit grain growth by dynamic recrystallization. It is suggested that thermal stability of the microstructure in Al alloys after severe plastic deformation plays a significant role in the occurrence of superplasticity. The relationship between precipitates, stability of microstructure, and superplasticity of several aluminum alloys after severe plastic deformation is discussed.

11:20 AM

Effect of Pressing Strain on the Annealing Behavior of Ultrafine Grained Ferrite in a Low Carbon Steel Fabricated by Equal Channel Angular Pressing: *Kyung-Tae Park*[1]; Dong Hyuk Shin[2]; [1]Hanbat National University, Div. of Adv. Matls. Sci. & Eng., San 16-1, Dukmyung-Dong, Yuseong-Gu, Taejon 305-719 S. Korea; [2]Hanyang University, Dept. of Metall. & Matls. Sci., 1271 Sa 1-Dong, Ansan, Kyunggi-Do 425-791 S. Korea

The annealing behavior of submicrometer order grained ferrite in a low carbon steel fabricated by equal channel angular pressing was investigated. In particular, the effect of the pressing strain on the annealing behavior of submicrometer order grained ferrite was examined by imposing two different pressing strains, 4 and 8. Contrary to the general fact that more severely worked materials exhibit faster kinetic of microstructural evolution related to annealing, i.e. recovery, recrystallization and grain growth, more strained steel exhibited more sluggish recovery and recrystallization kinetics under the present experimental conditions. It is suggested that more sluggish recovery and recrystallization kinetics with increasing the pressing strain is attributed to the combined effects of the release of the accumulated strain energy by formation of equilibrated structure and carbon dissolution from pearlitic cementite during pressing. The grain growth kinetics of submicrometer order grained ferrite was analyzed by applying the general description of the grain growth law. The grain growth exponent was about 0.2 and the activation energy for grain growth, 170-180 kJ/mol, was comparable to that for grain boundary diffusion of Fe in alpha-iron. Both values were not influenced by the pressing strain.

11:35 AM

Annealing Effect on the Strength of Severe Plastic Deformed Titanium: *Alla V. Sergueeva*[1]; Ruslan Z. Valiev[2]; Amiya K. Mukherjee[1]; [1]University of California, CHMS, 1220 Bainer Hall, Davis, CA 95616 USA; [2]Ufa State Technical University, Inst. of Phys. Of Adv. Matls., 12 Marx Str., Ufa 450000 Russia

Recent studies have shown that low temperature annealing (LTA) of severe plastic deformed (SPD) materials can lead to changes in the Hall-Petch relation slope without changing grain size. The nature and mechanisms of the strengthening are not clear yet. Mostly, the increasing in strength and hardness has been attributed to recovery processes. In present study it was shown that the maximum strength (1250 MPa) of SPD Ti can be achieved by short annealing at 250-300°C. The increasing temperature and/or time of thermal treatment lead to decreasing strength of the material. TEM observation revealed highly distorted structure within individual grains with non-uniform contrast in as-prepared state, whereas, the annealing results in full grain structure relaxation. But in this case, the highly non-uniform contrast of grain boundaries and near grain boundaries regions has been observed. The analysis of possible structural changes and their effect on the tensile properties has been presented. This investigation was supported by a grant from the US National Science Foundation (NSF-DMR-9903321).

11:50 AM

Effect of Refined Grain Size on the Shape Memory Behavior of NiTi Alloys Processed by ECAE: *I. Karaman*[1]; H. J. Maier[2]; H. Rack[3]; [1]Texas A&M University, Dept. of Mech. Eng., MS 3123, College Station, TX 77843 USA; [2]Universität Paderborn, Lehrstuhl f. Werkstoffkunde, Paderborn 33095 Germany; [3]Clemson University, Dept. of Cer. & Matls. Eng., Clemson, SC 29634 USA

Shape memory alloys have unique properties such as recoverability of deformation upon heating and pseudoelastic stress-strain behavior strains near 10%. To our knowledge, the effect of severe plastic deformation and the refined grain sizes below a micron has not been investigated to a great extent on the martensitic transformation that leads to pseudoelasticity and shape memory. The purpose of this study is to develop NiTi shape memory alloys (SMAs) with submicron grain sizes and to investigate the pseudoelasticity and shape memory characteristics in the presence of high volume fraction of interfaces. The materials chosen for this study are NiTi alloys with various compositions near equiatomic composition to control the phases present during selected processing routes and temperatures such as fully martensitic, fully austenitic and the mixture of martensitic and austenitic phases. The materials will be processed starting from coarse-grained precursors and processed by severe plastic deformation methods including equal channel angular extrusion (ECAE). ECAE will provide refined microstructure while conserving work piece geometry and some control over texture evolution. Several characterization techniques have been employed to identify resulting microstructure and mechanical behavior of the NiTi alloy produced. In this study, we will focus on four issues, namely (1) the effect of processing parameters on the resulting microstructures depending on the initial phase of the material (martensite or austenite), (2) the variation of transformation temperatures with the degree of deformation and the ECAE route, and (3) the monotonic tension and compression behavior in the pseudoelasticity and shape memory regions.

12:05 PM

Structure and Stability of Ultra-Fine Grain Materials: Role of Impurities and Second Phase Particles: *Nina Alexsandrovna Koneva*[1]; Anatolii Nikolaevich Zhdanov[1]; Nataliya Anatolievna Popova[1]; Evgenia Eduardovna Pekarskaya[1]; Eduard Victorovich Kozlov[1]; [1]Tomsk State University of Architecture and Building, Phys. Dept., Solyanaya Sq. 2, Tomsk 634003 Russia

The results of studied structure of ultrafine grained copper, nickel and alloys on their base, produced by severe plastic deformation(SPD), is generalized. There is a problem of real grains size, surrounded by large-angle boundaries. The sizes indicated are often underestimated. This questions is closely related to the anisotropy of grains, presence of subboundaries and structural texture of materials after SPD. Statistical analysis of distribution functions of sizes of grains and subgrains is performed. The problem of comparison of grain sizes, determined by

X-ray analysis and TEM, is discussed. Mechanisms of arising internal stress sources are analyzed. Role of grain boundaries, their joints and second phase particles is compared. SPD leads to redistribution of impurities in volume of metal. They are captured by dislocations and swept out primarily on grain boundaries and to joints of boundaries, where second phase particles are formed. The presence of particles is related to the problem of structure stability.

Surface Engineering: Science & Technology II: Oxidation/Corrosion/Nitridation

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

Program Organizers: Ashok Kumar, University of South Florida, Department of Mechanical Engineering, Tampa, FL 33620 USA; Yip-Wah Chung, Northwestern University, Department of Materials Science & Engineering, Evanston, IL 60208 USA; Gary L. Doll, The Timken Company, Canton, OH 44706 USA; D. S. Misra, Indian Institute of Technology-Bombay, Department of Physics, Powai, Mumbai 400076 India; John J. Moore, Colorado School of Mines, Department of Metallurgy and Materials Engineering, Golden, CO 80401 USA; Kryoshi Yatsui, Nagoka University of Technology, Nagaoka, Niigata 840-2188 Japan

Wednesday AM	Room: 203
February 20, 2002	Location: Washington State Conv. & Trade Center

Session Chairs: Gary L. Doll, The Timken Company, Canton, OH 44706 USA; S. V. Prasad, Sandia National Laboratories, Albuquerque, NM 87111 USA

8:30 AM Invited

Lower Thermal Conductive Thermal Barrier Coatings with Improved Cyclic Oxidation Life for Turbine Components: *Douglas E. Wolfe*[1]; *Jogender Singh*[1]; [1]Pennsylvania State University, Appl. Rsrch. Lab., PO Box 30, State College, PA 16804 USA

In order to produce lower thermal conductive thermal barrier coatings (TBC) that will allow higher engine operating temperatures, increased fuel savings, and longer component life, new coating materials and microstructural modifications are being considered. This paper discusses microstructural changes within the ZrO2-8wt.%Y2O3 (TBC) layer which dramatically lowered the thermal conductivity, while increasing the cyclic oxidation life of coated components. Altering the microstructure by introducing interfaces within the TBC has lead to a 20% reduction in the thermal conductivity and improved oxidation cyclic life (over 50%) of partially stabilized zirconia (ZrO2-8wt.%Y2O3) deposited by electron beam-physical vapor deposition on platinum-nickel-alumumide bond coated MAR-M-247. The traditional columnar microstructure of partially stabilized zirconia has been modified to produce a lower conductive TBC by periodically interrupting the condensing vapor and creating multiple interfaces. These interfaces serve as barriers for phonons, and thus decreases the thermal conductivity of the deposited coating. The thermal conductivity can further be controlled by controlling the distinctiveness and number of interfaces within the TBC layer. However, if the interfaces are too distinct, premature delamination of the layers may occur resulting in lower cyclic oxidation life. TBC samples were examined by various techniques including scanning electron microscopy (SEM), X-ray diffraction (XRD), electron probe microanalysis (EPMA), steady-state laser heat flux technique, and thermal cyclic tests. Multiple interfaced TBC exhibited better cyclic oxidation life with lower thermal conductivity as compared to conventional thermal barrier coatings (ZrO2-8 wt.%Y2O3).

8:55 AM

Factors Controlling In-Plane Cracking of Thermal Barrier Coatings: Zhehua Zhang[1]; Arne H. Swanson[1]; *Jun Kameda*[1]; Shigeo Sakurai[2]; Minoru Sato[3]; [1]Iowa State University, Ames Lab., 258 K Metals Dvlp., Ames, IA 50014 USA; [2]Hitachi, Ltd., Hitachi Work, Hatachi Japan; [3]Tohoku Electric Power Co., Ltd., Sendai 980 Japan

This paper summarizes a recent study on the in-plane cracking behavior near and away from the interface of thermally sprayed (PS) thermal barrier coatings (TBC) and thermally grown oxides (TGO) using a protruded TBC bend testing technique. The critical local tensile stress (σ^*) for in-plane TBC cracking near and away from the interface decreased and increased, respectively, with increasing substrate thickness. In order to examine how the formation of TGO and residual stresses control the in-plane TBC cracking, thermal ageing and cycling at 950°C in air were carried out. Near-interfacial cracks were initiated at slightly higher σ^* in aged specimens than in unaged specimens due to the sintering effect. The result indicates that the TGO formation itself does not cause the mechanical degradation of TBC without thermal cycling. The effect of thermal cycling on the in-plane TBC cracking is being examined to clarify the role of residual stresses.

9:10 AM

Developing a MoSi2+SiC Oxidation Resistant Coating for Mo a Prototype Refractory Metal: *Earl C. Hixson*[1]; [1]Colorado School of Mines, Metall., 920 16th St., Golden, CO 80401 USA

Refractory metals offer excellent high temperature mechanical properties, but lack sufficient oxidation resistance in air to see wide application. An oxidation resistant coating could potentially extend the usefulness of refractory metals at high temperature. Any coating system must have sufficient oxidation resistance and survive the thermal stresses of cycling between room temperature and 1600°C. The MoSi2+50wt% SiC coating system shows excellent oxidation resistance and matches the coefficient of thermal expansion of molybdenum. When combined with a Mo-Si-C-N containing diffusion barrier layer (DBL), the resulting coating system could successfully protect Mo from high temperature oxidation. Finite element models have been used to reduce the number of experiments and predict the stresses induced by thermal cycling. The finite element models have identified the DBL CTE as the critical variable in the coating stresses. Both FEM stress predictions and experimental oxidation and DBL crystallization studies will be summarized. Finally, an optimum coating architecture will be proposed.

9:25 AM

Development of Reactive Element Coatings to Improve H.T. Oxidation Performance of Iron-Chromium Alloys: *Lalgudi V. Ramanathan*[1]; Stela Maria Fernandes[1]; [1]Instituto de Pesquisas Energeticas e Nucleares-IPEN (Energy & Nuclear Rsrch. Inst.), Matls. Sci. & Tech. Ctr., Travessa R-400, Cidade Univ., Sao Paulo 05422-970 Brazil

The addition of small quantities of reactive elements (REs) to chromia and alumina forming alloys improves high temperature (HT) oxidation resistance. Traditionally, REs have been added to HT alloys in elemental form or as oxide dispersions. The REs can be also applied as coatings. The sol-gel technique is considered to be the most efficient and it generates nano-sized oxide particles. The effect of sol-gel processing parameters on RE particle size and morphology was determined. Various REs were studied and included: La, Nd, Ce, Pr, Dy, Y and Yb. Different techniques to coat alloy surfaces with RE sols were evaluated and spraying was found to be the most effective. The morphology of the coatings varied with the nature of the RE. The oxidation behavior of uncoated and RE coated specimens was evaluated from isothermal and cyclic oxidation tests. The extent to which the RE coatings influenced oxidation rate varied with oxide morphology and RE. Direct correlation between RE ion radius and extent of influence on chromia growth rate at 1000°C was obtained. The effect of applying secondary RE coats on the extent of protection was also determined gravimetrically and 3 RE oxides were selected (based on results from isothermal tests and cost). Based on results obtained in this investigation, an optimum procedure to protect chromia forming alloy components in HT oxidizing environments has been proposed.

9:40 AM

High Temperature Oxidation of Electrodeposited RE-Ni-W-P-SiC Multifunctional Composite: *Tongshun Fu*[1]; Zhongcheng Guo[2]; Shanli Ma[1]; Xiaoyun Zhu[2]; [1]China Great Wall Aluminium Company, Zhenzhou 450041 China; [2]Kunming University of Science and Technology, Fac. of Matl. & Metlgcl. Eng., Kunming 650093 China

The oxidation of the Multifunctional Electrodeposited RE-Ni-W-P-SiC Composites at high temperature is investigated. The results show that during high temperature oxidation the relationship between the mass change of pure Ni, Ni-W-P, Ni-W-P-SiC or RE-Ni-W-P-SiC coating and the oxidation time follows a mixed curve, i.e. it is approximately a linear relationship when the oxidation time is less than 60 mins while it is a power function relationship when the oxidation time is over 60 mins. The order for the oxidation rate of the four coatings is Ni> Ni-W-P> Ni-W-P-SiC>RE-Ni-W-P-SiC. The mass change of Ni-W-P, Ni-W-P-SiC or RE-Ni-W-P-SiC coating increases exponentially with a rise of oxidation temperature. The high temperature-oxidation resistance of RE-Ni-W-P-SiC composite coating is 3~4 times that of Ni-W-P alloy coating. The cross section morphologies and X-ray diffraction patterns indicate that the high temperature-oxidation resistance of RE-Ni-W-P-SiC composite coating is better than any other coatings.

9:55 AM Break

10:10 AM Cancelled
Investigation of a Low-Cost MOCVD Route for YSZ Thermal Barrier Coatings: *Susan Pran Krumdieck*

10:35 AM Cancelled
Oxidation Behavior of Bulk Dense Chromium Nitride Ceramics: *Hideyuki Kuwahara*

10:50 AM
The Corrosion Behavior of PVD-Grown WC-(Ti1-xAlx)N Films Superlattice in 3.5% NaCl Solution: *Seung-Ho Ahn*[1]; Yoon-Seok Choi[1]; Ji-Hong Yoo[1]; Jung-Gu Kim[1]; Jeon-Gun Han[1]; [1]SungKyunKwan University, Adv. Matls. Eng., 300, Chunchun dong, Jangan-Gu, Suwon 440-746 S. Korea

WC-(Ti1-xAlx)N coatings of constant changing Al concentration were deposited on S45C substrates by high-ionization sputtered PVD method. The Al concentration could be controlled by using evaporation source for Al and fixing the evaporation rate of the metals (WC alloy and Ti) (i.e., WC-Ti0.86Al0.14N, WC-Ti0.72Al0.28N, and WC-Ti0.58Al0.42N). The corrosion behavior of WC-(Ti1-xAlx)N coatings in deaerated 3.5% NaCl solution was investigated by electrochemical corrosion tests and surface analyses (EDS, XRD, AFM, and SEM). Particular attention was paid to the effects of Al target power density on the film properties related to the corrosion behavior. The measured galvanic corrosion currents between coating and substrate indicated that WC-Ti0.72Al0.28N coating showed the best resistance of the coating tested. The results of potentiodynamic polarization tests showed that the WC-Ti0.72Al0.28N coating deposited with 63W/§^{2} of Al target revealed higher corrosion resistance. This indicated that the WC-Ti0.72Al0.28N coating is effective in improving corrosion resistance. In EIS, the WC-Ti0.72Al0.28N coating showed one time constant loop and increased a polarization resistance of coating (Rcoat) relative to other samples.

11:05 AM Cancelled
Nitriding Behavior of Fe-Cr Alloys in the Temperature Range of 873-1073 K: *Hideyuki Kuwahara*

11:20 AM
Oxidation Behavior of Gama-TiAl Based Alloy Protected by Silicon Diffusion Treatment: *Xiang Yang Li*[1]; Y.-C. Zhu[1]; K. Fujita[1]; N. Iwamoto[1]; S. Taniguchi[2]; K. Nakagawa[3]; Y. Matsunaga[3]; [1]Ion Engineering Research Institute Corporation, 3rd Proj. Rsrch. Lab., 2-8-1, Tsuda-Yamate, Hirakata, Osaka 573-0128 Japan; [2]Osaka University, Dept. of Matls. Sci. & Eng., Grad. Sch. of Eng., 2-1 Yamadaoka, Suita, Osaka 565-0871 Japan; [3]Ishikawajima-Harima Heavy Industry, Tokyo 135-8732 Japan

Silicon diffusion treatment to improve the oxidation resistance of a ×-TiAl based alloy (Ti-48Al-1.3Fe-1.1V-0.3B at.%) was conducted by burying the specimen into Si powder and diffused at 800, 900 and 1000¢J for 2h and 5h in vacuum respectively. The isothermal oxidation behavior of the protected alloy was tested at 900¢J for 96h in air environment using a thermal balance. The element constitution, phase composition and morphology of Si modified layer and oxide scale were characterized by AES, XRD and SEM. The experimental results indicated that the oxidation resistance of the TiAl alloy was dramatically enhanced by Si diffusion treatment above 900¢J. The oxidation rate of 800¢J Si diffused alloy, however, is lower only in the beginning of the oxidation and accelerated shortly. It is found that Si rich layer was formed on the surface of the alloy and its thickness increased along with raising of the diffusion temperature. In addition, original surface phase of ×-TiAl was transformed into Ti5Si3 or other Si contained phases when the Si diffusion temperature higher than 900¢J, meanwhile, a layer rich in Si still remained in the oxide scale even after long-term oxidation in this case. It is concluded that the new phase such as Ti5Si3 formed on the surface of the alloy during Si diffusion treatment above 900¢J and the existence of the Si rich layer in the oxide scale contributed to the significant improvement of the oxidation resistance of TiAl based alloy.

11:35 AM
Electronoptical Observations for Electrical Breakdown Initiation of Anodic Films during Anodizing in Molten Bisulphate Melt: *Young Seog Kim*[1]; [1]Korean Institute of Industrial Technology, Ctr. of Tech. Dvlp. & Assistance for SMEs, 472. Ka Jwa Dong, Soo-Ku, Inchon 404-254 Korea

Anodizing of aluminium at constant current density in molten eutectic bisulphate melts results in the development of amorphous anodic alumina, which has been examined by TEM with EDX facilities and other analytical procedures. Over a wide range of anodizing conditions, barrier type anodic films are developed at high current efficiency at voltages below the dielectric breakdown voltage. The first sign of incipient breakdown revealed by transmission electron microscopy of stripped films, is always the appearance of dark regions about 1,000 nm in diameter, representing local overgrowth of the film. The breakdown mechanism is closely related to thermal effects, because temperature rises at regions representing local overgrowth in the stripped films were observed at voltages close to the breakdown voltage, likely arising through impact ionization. When impact ionization occurs at the low activation energy region of the aluminium substrate, i.e. grainboundary of substrate, then, motion of excessive activated positive ions(aluminium ion) from the substrate towards the film/electrolyte interface increases the resultant field strength across the film. This field enhancement process generates further electronic current at the film/electrolyte interface and increases the temperature in the film.

11:50 AM
A Process-Structure-Property Model for Nitrocarburising in a Fluidised Bed: *D. Fabijanic*[1]; G. L. Kelly[1]; P. D. Hodgson[1]; [1]Deakin University, Sch. of Eng. & Tech., Waurn Ponds, Victoria Australia

Nitrocarburising is a thermochemical treatment designed to diffuse nitrogen and carbon in to a ferrous substrate. Resulting is the formation of a hard, wear-resistant white layer (WL) above a tough diffusion zone (DZ). The WL consists primarily of the h.c.p. epsilon-Fe2-3(C,N) and f.c.c. gamma-Fe4N, while the DZ is a nitrogen-saturated iron matrix. This study aimed at establishing the relationship between process inputs and the resulting structure and properties of a nitrocarburised layer on various ferrous substrate materials. A Design of Experiment (DoE) was performed using a Taguchi L9 orthogonal array on four pertinent process parameters; temperature, time, nitriding potential and concentration of hydrochloric acid. Through subsequent surface characterisation a process-microstructure-property model for nitrocarburising in a fluid bed was established. This model is then used to control WL and DZ depths, WL phase composition and porosity structure and produce a surface treatment with properties desired for end use.

12:05 PM
Crystallization Process of Anodic Films during Post-Breakdown in the Molten Bisulphate Melt: *SungHo Han*[1]; [1]Korean Institute of Industrial Technology, Ctr. of Tech. Dvlp. & Assistance for SMEs, 472. Ka Jwa Dong, Soo-Ku, Inchon 404-254 Korea

The morphology and composition of anodic films, formed on aluminium at various current densities, in the range 1-100 A/m2, in the molten bisulphate melt at different temperatures(418-498K), have been studied using transmission electron microscopy of ultramicrotomed film sections and ion beam thinned films. When electropolished aluminium is oxidized anodically in the molten salt, the current density, I, through the anodic films shows a marked exponential dependence on the field, E, across the film. Furthermore, the dependence of the field strength on ln i at different temperatures, i. e. the Tafel slope, dE/d ln i, was found to be approximately constant with increase of temperature. The anodic films formed in the molten salt are generally barrier type and the current efficiency for film growth is approximately 100% until electrical breakdown occurs. The morphology and composition of the films formed on aluminium during post-breakdown in the molten salt have been studied by RBS and transmission electron microscopy of ultramicrotomed film sections and ion beam thinned films. On detailed examination of the anodic films, formed at 10 Am-2 in the molten salt, after breakdown for various times in the range 30 sec ¡- 20 min., two distinct phases were revealed; i. e. amorphous and crystalline alumina.

Teaching and Learning Hydrometallurgical Science and Engineering: Applied Hydrometallurgy/Thermodynamic Modeling

Sponsored by: Extraction & Processing Division, Aqueous Processing Committee, Copper, Nickel, Cobalt Committee, Precious Metals Committee, Waste Treatment & Minimization Committee
Program Organizers: Kwadwo Osseo-Asare, Pennsylvania State University, Metals Science and Engineering, University Park, PA 16802-5006 USA; Saskia Duyvesteyn, University of Utah, Department of Metallurgical Engineering, Salt Lake City, UT 84112-0114 USA

Wednesday AM — Room: 601
February 20, 2002 — Location: Washington State Conv. & Trade Center

Session Chairs: Kwadwo Osseo-Asare, Pennsylvania State University, Metals Sci. & Eng., 208 Steidle Bldg., University Park, PA 16802-5006 USA; Fiona M. Doyle, University of California, Dept. Matls. Sci. & Eng., 551 Evans Hall #1760, Berkeley, CA 94720-1760 USA

8:30 AM Keynote
Teaching and Learning Environmental Hydrometallurgy: *Fiona M. Doyle*[1]; [1]University of California, Dept. Matls. Sci. & Eng., 551 Evans Hall #1760, Berkeley, CA 94720-1760 USA

Environmental hydrometallurgy can be considered to comprise two distinctly different areas: environmentally compliant hydrometallurgy, and hydrometallurgy for environmental compliance. The latter includes both hydrometallurgical waste treatment and hydrometallurgical processes that can replace existing ones with attendant environmental benefits. This approach may find application in many fields well beyond those in which hydrometallurgy is traditionally encountered. Teaching environmental hydrometallurgy is truly coupled with learning, because this field is very much in its infancy. Students need a foundational knowledge base, but must learn to use these tools to think creatively, outside of the box. Cognizance of developments in other fields is also essential. Some of the most useful unit processes and new developments are discussed, such as biohydrometallurgy, ion exchange and membrane processes. These are examined as case studies that can be used to teach students to make future developments.

9:05 AM Keynote
Wet Chemical Processing in Integrated Circuit Manufacturing: *Srini Raghavan*[1]; [1]University of Arizona, Matls. Sci. & Eng., 147 Mines & Metallurgy, Tucson, AZ 85721 USA

The manufacturing of silicon based, high-speed integrated circuits (IC) involves a large number of wet chemical steps such as etching, rinsing, drying, plating and polishing. Principles of wet chemistry, electrochemistry and surface chemistry traditionally taught in hydrometallurgy courses can be effectively used to develop modules for a course in IC manufacturing. In this presentation, hydrometallurgical aspects of wet processing will be illustrated with two examples; copper contamination of silicon from hydrofluoric acid based solutions and chemical mechanical planarization (polishing) of copper. Opportunities for the development of environmentally benign processes using wet chemical principles will be discussed.

9:40 AM Invited
Teaching and Learning Adaptive Hydrometallurgy: *Batric Pesic*[1]; [1]University of Idaho, Col. of Mines, McClure Hall, Moscow, ID 83844-3024 USA

Hydrometallurgy spans many disciplines in the science, due to its chemistry, and technology, when particular reactions are put to use on a large, well engineered, physical scale. Speaking of physical scale of application, an additional trend is emerging, however. To many, the future and beyond belongs to the nanosized products. Although vast proportion of nanoproducts is prepared by the traditional hydrometallurgical methods, the chemical reactors and the accompanying tools, dramatically changed within the last decade. Hydrometallurgy does not belong to large physical scale any longer. Neither does it rely on chemistry alone; physics is of equal importance. The question arises regarding the teaching, if a new hydrometallurgy, nano-hydrometallurgy, curriculum should be established? If so, should it be on expense of traditional hydrometallurgy? The author will present his personal observations regarding hydrometallurgy in the US within academia, industry, and government, during the last twenty years, with his own view on dilemma to take the new nanoworld path.

10:05 AM Break

10:20 AM Invited
Utilization of an Equilibrium Calculational Program for Teaching Hydrometallurgy: Hsin-Hsiung Huang[1]; Courtney A. Young[1]; *Larry G. Twidwell*[1]; [1]Montana Tech of University of Montana, Metall. & Matls. Eng., 1300 W. Park, Butte, MT 59701 USA

Equilibrium calculational software programs can be effectively utilized to illustrate the importance of concentration, solubility, temperature, solution pH, solution potential, and ligand complexation to students studying hydrometallurgy. The calculational program STABCAL will be demonstrated. Illustrative examples for the creation of diagrams such as Eh-pH, concentration/solubility-pH and concentration/solubility-Eh will be developed to understand the fundamentals of real hydrometallurgical systems. Speciation, titration and mixing will be used to simulate or predict operational processes. Applications will include treatment of Acid Mine Drainage (Berkeley Pitlake water, in particular), leaching and selective separation of metals from electroplating sludge, and flowsheet development fortreating mercury sulfide K106 sludge.

10:45 AM Invited
Aqueous Stability Diagrams for Process Design and Analysis: The ABC Approach: *Kwadwo Osseo-Asare*[1]; [1]Pennsylvania State University, Dept. of Matls. Sci. & Eng., Steidle Bldg., University Park, PA 16802 USA

A systematic method is presented for using aqueous stability diagrams as engineering tools. For a diagram of the type Eh vs. pH (i.e. Eh-pH or Pourbaix diagram), three aqueous stability domains (lakes) are recognized and labeled as A, B, C, for acidic, basic, and complexing regions respectively. Dissolution or precipitation reaction paths are identified by linking the lakes and the adjacent solid phase stability regions (hills) with corresponding chemical equations. Flowsheets are then developed by using the reactants and products of the reaction path equations as feed and product materials for the respective unit process (e.g. dissolution or precipitation). Additional concepts such as dissolution/precipitation, selectivity, and redox windows are introduced and illustrated with examples. Combined hydrometallurgical/pyrometallurgical processing is also addressed.

11:10 AM Invited
Teaching Computational Thermodynamics: Wet Flue-Gas Scrubber for Power Plants and Metallurgical Furnaces: *Y. K. Rao*[1]; [1]University of Washington, Dept. of Matls. Sci. & Eng., Box 352120, Seattle, WA 98195 USA

The computation of equilibrium-state is illustrated by the flue-gas-scrubbing operations that use a slurry of lime/limestone and freshwater to convert sulfur oxides (SO2+SO3) to solid products CaSO4.2H2O and CaSO3.0.5H2O. The equilibrium compositions and the respective amounts of the gaseous, aqueous and solid phases that occur in the five-phase heterogeneous (Ca-O-C-H-S-N-Cl) system are computed by means of the iterative equilibrium constant method; the number of species (gaseous, condensed, aqueous ionic and aqueous non-ionic) exceeds thirty. The flue-gas entering the scrubber may contain CO2, O2, N2, H2O(g), NO, N2O, SO2, SO3, and HCl. The computation is presented for 25°C and 101.325 kPa or 1 atm pressure.

11:35 AM Invited
Chemical Modeling of High Temperature Aqueous Processes: *Haixia Liu*[1]; Vladimiros G. Papangelakis[1]; [1]University of Toronto, Dept. of Cheml. Eng. & Appl. Chem., 200 College St., Toronto, Ontario M5S 3E5 Canada

Chemical modeling constitutes a very powerful tool to predict and understand the behavior of complex aqueous processing systems. Needless to add is the educational aspect associated with building such models. In recent years, chemical modeling has undergone tremendous development. The new capabilities of various software have changed the way scientists approach the objective to simulate aqueous solutions in hydrometallurgical process. This paper presents new developments and strategies to simulate high temperature aqueous processing systems. The acid pressure leach of nickeliferous laterites is used as an example. Calculation of standard thermodynamic properties of aqueous species was performed with the revised Helgeson-Kirkham-Flowers (HKF) model as well as with the Density model. Nonidealities, including weak ion pair formations, were treated through the Bromley-Zemaitis ion interaction method. The above models were implemented through the OLI-Systems-μ Commercial software. Pure binary solutions like Al2(SO 4)-H2SO4, MgSO4-H2SO4, NiSO4-H2SO4,Fe2O3-H2SO4 were modeled first followed by progressively more complex solution mixtures. Finally, simulation results were compared with available experimental solubility data and very good agreement was found.

Third International Sulfide Smelting Symposium - "Sulfide Smelting '02": Furnace Integrity and Smelting Slags

Sponsored by: Extraction & Processing Division, Pyrometallurgy Committee, Copper, Nickel, Cobalt Committee, Lead, Zinc, and Tin Committee, Non-Ferrous Metals Committee
Program Organizers: Robert L. Stephens, TeckCominco Metals, Ltd., Trail, British Columbia V1R 4L8 Canada; Hong Yong Sohn, University of Utah, Department of Metallurgical Engineering, Salt Lake City, UT 84112 USA

Wednesday AM	Room: 607
February 20, 2002	Location: Washington State Conv. & Trade Center

Session Chairs: Mineo Hayashi, Mitsubishi Materials Corporation, Process & Tech. Dept. Met. Co., 1-5-1 Ohtemachi Chiyoda-ku, Tokyo 100-8117 Japan; David B. George-Kennedy, Kennecott Utah Copper Corporation, 8315 West 3595 S., PO Box 6001, Salt Lake City, UT 84044-6001 USA

8:30 AM
Kennecott Flash Converting Furnace–Design Improvements 2001: *Chris J. Newman*[1]; Matthew M. Weaver[1]; [1]Kennecott Utah Copper Corporation, Copper Smelter, 12000 W. 2100 S., PO Box 329, Magna, UT 84044 USA

In January 1999, a redesign of the Kennecott Flash Converting furnace settler was initiated to enhance furnace integrity and extend furnace life. A detailed assessment was made of all technology available around the world before making a decision on the design features to be incorporated in the new design. The new design includes the following: redesign of all sidewall cooling elements to include the latest cooling element technology; redesign of the furnace hearth to include a stadium hearth at the reaction shaft end of the furnace; redesign of the furnace hearth to include a stepped hearth design adjacent to the furnace side walls; addition of flat settler roof cooling elements around the reaction shaft; replacement of reaction shaft transition elements with an improved design and improvements to the furnace cooling element monitoring systems. The Flash Converting furnace was shut down on a planned basis in July 2001 to implement these improvements after 29 months of operation, converting more than 1,000,000 tonnes of matte. During the 30 day shut down, the improvements were successfully implemented, with furnace start up in August 2001.

9:05 AM
Improved Technology for Water-Cooled Copper Blocks: *Allan MacRae*[1]; [1]Kvaerner Metals E&C, 12657 Alcosta Blvd., Ste. 200, San Ramon, CA 94583 USA

A new copper alloy for coils in cast copper cooling blocks has been identified and samples prepared for metallurgical examination and destructive testing to compare with cast cooling blocks manufactured from copper and nickel-copper (NiCu) alloy pipes. The new copper alloy allows for the formation of a metallurgical bond between the pipe and the cast copper during the casting process, which does not normally occur with pure copper or nickel-copper alloy pipes. The alloy's coefficient of thermal expansion is also much closer to that of pure copper compared with NiCu alloys, so there is less strain induced at the pipe-cast copper interface due to differential thermal expansion. It is expected that this new pipe coil alloy and associated casting techniques (Patents Pending) will allow for the production of cast copper cooling blocks that have greatly enhanced service life in high heat load applications compared to existing technologies.

9:30 AM
Current Practice in Taphole Design: *Melissa Trapani*[1]; Andrew Kevin Kyllo[1]; Neil B. Gray[1]; [1]The University of Melbourne, Dept. of Cheml. Eng., Parkville, VIC 3010 Australia

The removal of molten products from metallurgical furnaces is one of the most hazardous and labour intensive processes in a non-ferrous smelter. The proximity of operators to the molten metal and slag during tapping and the oxygen lancing that facilitates the flow have led to many reported injuries on tapping floors. In most cases, tapholes are opened and closed periodically leading to extreme thermal cycling in the tapping assembly. Consequently, refractory wear rates are high and unpredictable in the taphole. This paper provides a review of the current state of taphole development, and gives a methodology which is now being applied to gain a better understanding of the taphole region, to allow design improvements.

9:55 AM
Non-Isothermal Study of Refractory Dissolution by Copper Containing Calcium Ferrite Slag: *Kim Fagerlund*[1]; Tuija Suortti[1]; Pekka Taskinen[1]; [1]Outokumpu Research Oy, PO Box 60, Pori FIN-28101 Finland

A novel method for studying refractory erosion and dissolution/degradation under a temperature gradient was developed. To overcome conventional isothermal refractory testing, a new "cold finger" technique, based on a crucible test with a cooling element, has been developed to provide practical information on penetration and dissolution of refractory materials under cooled conditions. This technique was adopted and applied to several refractory-slag systems. Commercially available magnesia chrome refractory bricks against copper containing calcium ferrite type of slag were tested and compared using both a conventional crucible test and the new cooling method. The experiments were conducted between 1300-1420°C under a controlled atmosphere of nitrogen or air. It was noticed, that the type of porosity had a significant effect on penetration of magnesia chrome refractories. Furthermore, the copper containing calcium ferrite slag caused severe slag attack and refractory failure in some cases, due to its fluidity and corrosive nature. Characteristics of the penetration and dissolution mechanisms were analyzed from the sample microstructures.

10:20 AM Break

10:35 AM Cancelled
Wear of Magnesia-Chrome Brick in PS Converter: *Yongfeng He*

11:00 AM
Slags of Suspension Smelting of Chalcopyrite Ores and Copper Matte Converting: Heikki Jalkanen[2]; *Jaakko Poijarvi*[1]; Hanna Pajari[3]; [1]Outokumpu Harjavalta Metals Oy, Teollisuuskatu 1, Harjavalta FIN-29200 Finland; [2]Helsinki University of Technology, Lab. of Metall., Vuorimihentie 2, PO Box 6200, Espoo FIN-02015 Finland; [3]Outokumpu Pori Copper Oy, PO Box 60, Pori FIN-28101 Finland

The slag formation mechanisms in suspension smelting and matte converting affect the composition and properties of molten and solidified slags. The final mineralogical composition and morphology of solidified slags, that is of great importance for slag cleaning by froth flotation, results from the state of molten slag before solidification and processes taking place during solidification and cooling. In suspension smelting, oxidation processes take place in the reaction shaft whereas final slag and matte forms in the settler due to reactions of condensed oxidation products and slag forming agents. During slag solidification and cooling, copper and sulfur dissolved in the molten slag are rapidly precipitating in metallic or sulfide form and metals present in the raw materials are distributed in a distinct manner between soldified slag and non-silicate solidification products. Smelting and converting slags differ remarkably in their mineralogical composition and morphology despite resulting principally from the same chemical processes. Slag forming, solidification, and precipitation phenomena are discussed on the basis of mineralogical and morphology analyses of smelter slags and laboratory scale experiments.

11:25 AM
Trends in Development of Autogenous Smelting of Sulfide Materials using Oxygen-Flame Smelting Processes: V. M. Paretsky[1]; *Andrey V. Tarasov*[1]; [1]State Research Institute of Non-Ferrous Metals "Gintsvetmet", 13, Acad. Korolyov St., Moscow 129515 Russia

There are many technical, economic, and environmental advantages to be gained by the use of a single-stage process for production of white metal. However, the changeover to a single-stage smelting process for the production of white metal requires solutions to a number of technical issues, the most serious of which is the requirement for a more stringent approach to selection of slag compositions. This approach should be based on the following major principles: homogeneity of high iron slags with high Fe^{3+}, selection of a slag composition with a new distribution of copper between white metal and slag, the need to process gold-bearing quartz flux for most smelters, the formation of slags well-suited for subsequent slag cleaning, and selection of an appropriate furnace design taking into consideration the high reactivity of the slags. At the Gintsvetmet Institute, two single-stage processes have been developed for the production of white metal and highly basic slag, including both the processing technology and the required equipment. They are based on the oxygen-flame smelting technology well suited for autogenous smelting with production of calcium ferrite slags. These versions are the oxygen-flame smelting process (KFP Process), currently being introduced at the Kovoguty Krompahy Smelter (Slovakia) and the flame-type sparged smelting process (FBP Process) being introduced at the ALmalyk Copper Smelter

(Uzbekistan). In order to provide a more rigorous basis for selection of slag compositions for autogenous smelting processes, researchers at the Gintsvetmet Institute conducted studies into the compositions and structures of slags produced on a semi-commercial scale as a result of KFP and FBP processes, as well as slag from a full-scale KFP furnace in Almalyk. The studies were carried out with the aid of mineralogical microscopy, Cameca microprobe analyses, and nuclear gamma-resonance spectroscopy. Solidified and quench slags were investigated with different cooling rates of 10^{3}°C/s (bar samples) and 10^{6}°C/s (superfast quenching by spinning-disc method). In the latter case, the structure of liquid slag was preserved (super-cooled liquid) permitting a more definite assessment of the true structure of slag in the molten state. The results obtained make it possible to give certain recommendations with respect to reduction in copper loss in slags in autogenous smelting processes.

Water Vapor Effects on Oxidation of High-Temperature Materials: Alloys III

Sponsored by: ASM International: Materials Science Critical Technology Sector, Structural Materials Division, Corrosion and Environmental Effects Committee
Program Organizers: Peter F. Tortorelli, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6156 USA; Karren L. More, Oak Ridge National Laboratory, Metals and Ceramics Division, Oak Ridge, TN 37831-6064 USA; Elizabeth J. Opila, NASA Glenn Research Center, Cleveland, OH 44135 USA

Wednesday AM	Room: 305
February 20, 2002	Location: Washington State Conv. & Trade Center

Session Chairs: B. Gleeson, Iowa State University, Ames, IA 50011 USA; W. J. Quadakkers, Forschungszentrum Jülich, Jülich 52425 Germany

8:30 AM
The Effect of Moisture on Secondary Spallation of Alumina Scales on Y-Doped Rene'N5: *James L. Smialek*[1]; [1]NASA Glenn Research Center, Matls. Div. 106-1, 21000 Brookpark Rd., Cleveland, OH 44135 USA

The single crystal superalloy Rene'N5 (with and without Y-doping or hydrogen annealing) was cyclically oxidized at 1150°C for 1000 hours. Primary spallation was observed for un-doped, un-annealed samples. However, after considerable scale growth (500 hr.), even the adherent alumina scales formed on Y-doped samples exhibited secondary delayed interfacial spallation during subsequent water immersion tests. Spallation was monitored by weight change and image analyses of the area spalled to bare metal. Hydrogen annealing (prior to oxidation) reduced spallation both before and after immersion, but without measurably reducing the bulk sulfur content of the Y-doped alloys. Only the carbon content was measurably reduced, which may account for the increased scale adhesion upon hydrogen annealing. The strain energy released was followed by acoustic emission, indicating a rapid succession of crack growth bursts ~1 m/s. A proposed failure method is proposed in which a contaminated interface allows moisture ingress and a local decrease in interfacial toughness.

9:00 AM
Effect of Water Vapor on the Oxidation Behavior of Alumina and Chromia Forming Superalloys: *K. Onal*[1]; G. H. Meier[1]; F. S. Pettit[1]; [1]University of Pittsburgh, Matls. Sci. & Eng., 848 Benedum Hall, Pittsburgh, PA 15261 USA

The oxidation behavior of several alumina and chromia forming superalloys have been examined and compared for dry air and wet air at 900°C and 700°C, both under cyclic and isothermal conditions. The results show that water vapor causes the oxidation of the alloys to be increased during cyclic exposures. The scale adherence is also affected by cyclic exposures, especially in the presence of water vapor. Under these conditions substantial amounts of oxide spallation are observed, whereas isothermal exposures in air with steam do not show the same effect. Possible mechanisms for these effects of water vapor will be proposed.

9:30 AM
Effects of Water Vapor on the High-Temperature Oxidation of Alumina-Forming Coatings and Ni-Base Superalloys: *M. C. Maris-Sida*[1]; G. H. Meier[1]; F. S. Pettit[1]; [1]University of Pittsburgh, Matls. Sci. & Eng., 848 Benedum Hall, Pittsburgh, PA 15261 USA

Superalloys develop oxidation resistance by forming protective scales of alumina or chromia during exposure to oxidizing conditions. As has been presented in the literature, water vapor has been observed to deleteriously affect the oxidation of superalloys. Isothermal oxidation experiments have been performed on a number of Ni base superalloys and coatings on these alloys in dry air and air saturated with water vapor (=0.05, 0.1 and 0.5 atm) for short times (10 minutes and 1 hour at 1100°C). Also, cyclic oxidation exposures under the same conditions were carried out for several hundreds of cycles. Results from these experiments show that the high temperature oxidation of superalloys is influenced by water in the gaseous state in two important ways: the oxide scales crack and spall sooner in air containing water vapor; and the development of continuous alumina scales is inhibited in a water vapor environment. Mechanisms will be proposed for these observed effects.

10:00 AM
High Temperature Oxidation Behavior of Some Superalloys in Steam Environment: *V. Desai*[1]; D. Tamboli[2]; [1]University of Central Florida, AMPAC, 12443 Research Pkwy., Ste. 404, Orlando, FL 32826 USA; [2]Ashland Specialty Chemical Company, R&D, 5200 Blazer Pkwy., Dublin, OH 43017 USA

For land based gas turbines, steam cooling hot gas path components offers many advantages over conventional compressed air cooling. However, superalloys are not designed to operate in steam environment at high temperatures and understanding oxidation behavior of these alloys at high temperatures warrants attention. Three superalloys with varying low to high Al content were subjected to short and long-term high temperature oxidation in flowing steam conditions, slightly above atmospheric pressure. Moderate Al content alloy showed considerable internal oxidation, weight loss and non-steady behavior even after a long exposure period. This study indicated different oxidation characteristics in steam compared to that in air. In particular, it was determined that the transition of these alloys (moderate Al content) from Chromia forming (non-protective) to Alumina forming (protective) alloy was prolonged. X-ray photoelectron spectroscopy of the surface oxide revealed a chemical difference in the air formed and steam formed oxide.

10:30 AM
Effects of Water Vapor on Oxidation of Chromium Containing Alloys at 2000°F: *M. J. McNallan*[1]; Y. S. Park[2]; [1]University of Illinois, CME Dept., MC 246, 842 W. Taylor St., Chicago, IL 60607 USA; [2]Haynes International, Eng. & Tech. Grp., 1020 W. Park Ave., PO Box 9013, Kokomo, IN 46904-9013 USA

The presence of water vapor in oxidizing environments can affect the oxidation kinetics of alloys by increasing the formation of volatile species. The effect of increasing water vapor content in 5% increments from dry air to air containing 20% water vapor has been investigated for three nickel based alloys and a cobalt based alloy, all of which obtain oxidation resistance from formation of chromium oxide scales (Alloy X, Alloy 617, Alloy 188, and Alloy 230). Long term tests were performed at 2000°F with temperature cycles to room temperature at 1008-hour intervals. Both weight changes and internal attack characterization are reported. The effects of alloy composition on the behavior are discussed.

11:00 AM
Role of Water Vapour in Chromia Scale Growth at Low Oxygen Partial Pressure: *David J. Young*[1]; [1]University of New South Wales, Sch. of Matls. Sci. & Eng., Sydney, NSW 2052 Australia

The oxidation behaviour of pure chromium and ODS-Cr alloys in Ar-H_2-H_2O and Ar-O_2-H_2O was studied at 1000°C. At high oxygen potentials, the addition of H_2O to the gas had negligible effect on scaling behavior. However, at low oxygen potentials, when the $PH_{20}PH_2$ ratio was held constant, the oxidation rate increased with water partial pressure. Increasing values of $PH_{20}PH_2$ led to more rapid rates. At fixed PH_{20} values, the rate increased with increasing PH_2. Compact scales were formed under all conditions. In addition Cr_2O_3 blades grew on the scale surface when pure chromium was reacted with H_{20}/H_2 mixtures but not in reaction with O_2H_2O. These blades did not form when Y_2O_3 dispersion strengthened material was reacted. Detailed consideration of local equilibrium between H_2O(g) and Cr_2O_3(s) led to the conclusions that oxide growth was sustained by diffusion of chromium vacancies and that adsorption of H_2O on oxide exposed to low oxygen activity gas led to formation of hydroxyl species. This model is shown to be consistent with the complex effects of gas composition on scale growth and blade formation.

11:30 AM
Water Vapor and Oxygen/Sulfur Impurity Effects on Simultaneous Oxidation and Nitridation in Cr2Nb Laves Phase Reinforced Cr: M. P. Brady[1]; *P. F. Tortorelli*[1]; L. R. Walker[1]; [1]Oak Ridge National Laboratory, Metals & Cer., MS 6115, Oak Ridge, TN 37831-6115 USA

The oxidation and nitridation behavior of Cr(Nb) solid solution and intermetallic Cr2Nb Laves phase was studied individually and in combination at 950°C or 1100°C in dry air, humid air, and N_2-$4H_2$. Greatly increased subscale nitridation was observed in Cr_2Nb-matrix alloys exposed at 950°C in both dry and humid air when the starting levels of oxygen and sulfur impurities in the alloys were reduced. At 1100°C, little effect of alloy impurity level was evident; however, exposure of Cr_2Nb-matrix alloys in humid air resulted in greatly increased subscale nitridation as compared with exposure in dry air. Pure Cr and Cr(Nb) solid solution alloys were relatively insensitive to water vapor or impurity oxygen/sulfur effects under the conditions studied. Possible synergistic effects between sulfur and water vapor and the beneficial role sulfur may play in reducing Cr_2O_3 scale permeability to nitrogen are discussed.

Advances in Metallic Glasses: Mechanical and Other Physical Properties, and Applications - II

Sponsored by: Electronic, Magnetic & Photonic Materials Division, *Program Organizers:* K. F. Kelton, Washington University, Department of Physics, St. Louis, MO 63130 USA; A. L. Greer, University of Cambridge, Department of Materials Science & Metallurgy, Cambridge CB2 3QZ UK; Krishna Rajan, Rensselaer Polytechnic Institute, Department of Materials Science and Engineering, Troy, NY 12180-3590 USA

Wednesday PM	Room: 212
February 20, 2002	Location: Washington State Conv. & Trade Center

Session Chairs: Daniel B. Miracle, Air Force Research Laboratory, Matls. & Mfg. Direct, 2230 Tenth St., AFRL/MLLMD, Dayton, OH 45433 USA; David A. Rigney, The Ohio State University, Matls. Sci. & Eng., 2041 College Rd., Columbus, OH 43210 USA

2:00 PM
High Temperature Deformation Behaviors of the Bulk Metallic Glass $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ Alloy: *Kwang Seok Lee*[1]; Tae Kwon Ha[1]; Sangho Ahn[2]; Young Won Chang[1]; [1]Pohang University of Science and Technology, Ctr. for Adv. Aeros. Matls. (CAAM), Pohang 790-784 S. Korea; [2]Research Institute of Industrial Science and Technology, Matls. & Proc. Rsrch. Ctr., Pohang 790-600 S. Korea

We have examined the deformation behaviors of a $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ bulk metallic glass that has a wide supercooled liquid region over 100K before crystallization. In compression testing in the supercooled liquid region, two types of nominal stress-strain curves were obtained. At near T_g and at strain rates higher than 10^{-3} s^{-1}, the metallic glass were fractured at maximum stress without plastic deformation. But at temperatures ranging from 401°C to 431°C, plastic deformation has been shown at strain rates ranging from $2x10^{-4}$ s^{-1} to $2x10^{-2}$ s^{-1}. Applying these compression test conditions to tensile test, superplastic deformations with maximum elongation over 500% have been observed at relatively high strain rate of $2x10^{-2}$ s^{-1} at the temperatures ranging from 401°C to 431°C. However, at the same initial strain rate, the test samples were observed to exhibit brittle fracture at the temperatures below T_g and above T_x. The superplastic properties such as flow stress and elongation were found to be very sensitive to test temperature and initial strain rate. DSC, XRD and TEM analysis for the mechanically tested specimens have been performed to investigate the changes of microstructure, thermal stability and crystallization behavior during deformations with various test conditions.

2:20 PM
Comparison of Fatigue Behavior of a Zirconium Based Bulk Amorphous Metal in Vacuum and Air: *William Hutchison Peter*[1]; R. Buchanan[1]; C. T. Liu[2]; P. Liaw[1]; [1]University of Tennessee, Matls. Sci. & Eng. Dept., 227 Dougherty Engineering Bldg., Knoxville, TN 37996-2200 USA; [2]Oak Ridge National Laboratory, Metals & Cer. Div., PO Box 2008, MS 6115, Oak Ridge, TN 37831-6115 USA

Exciting recent advances have led to "bulk amorphous materials" (BAMs) with fabrication diameters as large as 20 mm. Although the mechanical behavior of BAMs has been studied, fatigue characteristics in controlled environments has not been well performed. Early fatigue studies have resulted in fatigue strengths lower than anticipated. It is suspected that environmental effects degrade the fatigue life. Fatigue testing of zirconium-based bulk metallic glass has been performed in a 3.5% NaCl electrolyte at room temperature. Results of these tests have shown a substantial decrease in fatigue lifetimes when compared with those from tests conducted in air. The next step toward understanding the corrosion-fatigue phenomenon is to compare fatigue results in air and vacuum. This comparison will define any detrimental effects of humidity on fatigue lifetime of a Zr-based BAM. This research was jointly sponsored by the NSF Integrative Graduate Education and Research Training (IGERT) Program on "Materials Lifetime Science and Engineering" (DGE 9987548) and the Division of Materials Sciences and Engineering, US DOE under contract DE-AC05-OR22725 with UT-Battelle, LLC.

2:40 PM
Cyclic Deformation Behavior and Fatigue Fracture of Bulk Zr-Al-Ni-Cu Metallic Glass with Fully Amorphous and Partially Crystalline Structures: *Zhang Hai Feng*[1]; Zhang Qing Sheng[1]; Wu Shi Ding[1]; Ding Bing Zhe[1]; Hu Zhuang Qi[1]; [1]Institute of Metal Research, Shenyang Natl. Lab. for Matls. Sci., Wenhua Rd. 72, Shenyang, Liaoning 110016 China

This work is an investigation of cyclic deformation behavior and fatigue fracture of a bulk amorphous alloy with quenched-in crytallites. Experimental measurements indicated that fully amorphous alloy was absence of cyclic hardening or softening. For the bulk amorphous alloy with fine quenched-in crystallites had the same mode as fully amorphous alloy, neither cyclic hardening nor cyclic softening. The netlike array of shear bands for amorphous specimen. The fatigue crack initiation occurred on the surface for the fully amorphous alloy and specimen with fine crystallites. However, for the specimen with larger crystallites the crack originated from a big broken crystallite near the surface. The striation pattern on the amorphous matrix differed from that on the surface of crystallites. The average striation spacing on amorphous area was much larger than that on the crystallite.

3:00 PM
Effects of Hydrogen and Open-Volume Defects on Deformation and Fracture Behavior of Zr-Ti-Ni-Cu-Be Bulk Metallic Glass Alloys: *Daewoong Suh*[1]; Reinhold Dauskardt[1]; [1]Stanford University, Dept. of Matls. Sci. & Eng., Stanford, CA 94305-2205 USA

The effects of hydrogen and open-volume defects (free volume) on deformation and fracture behavior of Zr-Ti-Ni-Cu-Be bulk metallic glass alloys (Vitreloy 1) are presented in an attempt to better understand mechanisms for flow and fracture of metallic glasses. A range of thermomechanical behavior, including viscoelastic deformation, hardness, fracture, fatigue crack growth, glass transition and crystallization kinetics are examined with varying amounts of hydrogen and open-volume defects. The nanoscale structure of the metallic glass was examined using positron annihilation spectroscopy, high-resolution transmission electron microscopy, small-angle X-ray and neutron diffraction, and X-ray photoelectron spectroscopy. It was found that hydrogen charging and low temperature annealing increased the time scale for viscoelastic relaxation in the amorphous microstructure, both leading to sluggish atomic relaxation behavior and severe embrittlement. The reduced atomic mobility is believed to suppress stress relaxation at crack tips and hence induce brittle fracture behavior. Both hydrogen charging and annealing result in changes in the distribution of open-volume defects. Such changes are discussed in an attempt to elucidate the fundamental mechanisms of deformation and fracture.

3:20 PM Break

3:40 PM
Sliding of Metallic Glass: Experiments and MD Simulations: *David A. Rigney*[1]; Xi-Yong Fu[2]; Michael L. Falk[3]; [1]The Ohio State University, Matls. Sci. & Eng., 2041 College Rd., Columbus, OH 43210 USA; [2]Merck Research Laboratories, WP78-304, Sumneytown Pike, West Point, PA 19486 USA; [3]University of Michigan, Matls. Sci. & Eng., & Appl. Phys., Ann Arbor, MI 48109-2136 USA

The sliding behavior of metallic glass was studied using simple pin-on-disk tests and molecular dynamics (MD) simulations. Friction coefficients and wear rates of a Zr-Ti-Cu-Ni-Be alloy were similar to those reported for ductile materials, e.g., normal crystalline metals. Sliding caused plastic deformation, transfer, mechanical mixing and reamorphizing of devitrified material. In vacuum, a softer layer developed adjacent to the interface. In air, an additional harder layer appeared when oxidation products mixed in. MD simulations involved a two-component 2D amorphous system. Simulations of tensile tests showed elastic/perfectly plastic response, strain rate dependence and void formation. Simulations of sliding showed decreased density near the interface, suggesting an increase in free volume during shear, but no void formation. Subsurface displacement profiles were similar to those reported in experiments on crystalline materials and were consistent with flow patterns expected for flow near a boundary. The MD results on mechanical mixing suggest relevance to other processes, including mechanical alloying, friction welding, formation of nanocrystals, erosion and deformation at very high strain rates.

4:00 PM

An Instrumented Indentation Study of Mechanical Deformation in Bulk Metallic Glass: *Raj Vaidyanathan*[1]; Ming Dao[2]; G. Ravichandran[3]; Subra Suresh[2]; [1]University of Central Florida, AMPAC & MMAE, 12443 Research Pkwy., Ste. 404, Orlando, FL 32826 USA; [2]Massachusetts Institute of Technology, Dept. of Matls. Sci. & Eng., Rm. 8-139, 77 Massachusetts Ave., Cambridge, MA 02139 USA; [3]California Institute of Technology, Div. of Eng. & Appl. Sci., 1200 E. California Blvd., Pasadena, CA 91125 USA

Instrumented sharp indentation experiments at the nano- and micro-length scales were carried out in an attempt to quantify the deformation characteristics of a bulk metallic glass. The experiments were accompanied by detailed three-dimensional finite element simulations of instrumented indentation to formulate an overall constitutive response. By matching the experimentally observed continuous indentation results with the finite element predictions, a general Mohr-Coulomb type constitutive description was extracted to capture the dependence of multiaxial deformation on both shear stresses and normal stresses. Constrained deformation of the material around the indenter results in incomplete circular patterns of shear bands whose location, shape and size are captured well by the numerical simulations. The surface deformation features are also consistent with mechanisms such as localized shear flow, serrated yielding and adiabatic heating, which are observed during macroscopic mechanical tests.

4:20 PM

Deformation Behavior of Bulk Ni-Based Glass Composites Containing a Ductile Metal Synthesized by Warm Extrusion of Gas Atomized Powders: *D. H. Bae*[1]; M. H. Lee[1]; E. Rozhkova[2]; D. Sordelet[2]; D. H. Kim[1]; W. T. Kim[3]; [1]Yonsei University, Metlgcl. Eng., 134, Shinchon-dong, Seodaemum-ku, Seoul 120-749 Korea; [2]Iowa State University, Matls. Sci. & Eng., 107 Metals Development, Ames, IA 50011 USA; [3]Chonju University, Phys., 36 Naedok-dong, Chonju 360-764 Korea

Ductile metal reinforced metallic glass matrix composites are prepared by warm extrusion of gas atomized powders for the purpose of improving ductility of the monolithic metallic glass. A mixture of amorphous $Ni_{59}Zr_{20}Ti_{16}Si_2Sn_3$ powders and ductile metal powders, either Cu or low-carbon steel, were extruded in the supercooled liquid region of the amorphous powder with an extrusion ratio of 5. The volume fraction of ductile metal ranged between 0 and 30%. After extrusion all powders were elongated along the extrusion direction; no porosity was visible. The extruded materials were tested under uniaxial compression. Samples containing a ductile phase exhibited slightly lower fracture strengths (e.g., to 1.85GPa for 10 vol% of Cu compared to 2.0 GPa for 0 vol%). Ductility of the composite is improved as the volume fraction of ductile metal increases due to effect on stabilization against shear localization and crack propagation. Further detailed deformation mechanism in the composite will be presented.

4:40 PM

The Role of Structural Relaxation in the Plastic Flow Behavior of Metallic Glasses: *Vitaly Khonik*[1]; [1]State Pedagogical University, Dept. of Gen. Phys., Lenin St 86, Voronezh 394043 Russia

Plastic flow of metallic glasses (MGs) is crucially dependent on the kinetics of irreversible structural relaxation (SR). For samples stored at room temperature after production, the rate of structural relaxation is very low at temperatures $T < 300$ to 400 K and maximal at $T > 400$ K. Correspondingly, one can distinguish two stages of irreversible SR: the stage of "slow" SR and the stage of "fast" SR. Several experiments show that MGs' plastic behavior under the "slow" SR stage closely resembles localized flow of crystals being deformed via the dislocation mechanism. In particular, predeformed samples display a number of dislocation-like relaxations. Plastic deformation of MGs under the "fast" SR stage is homogeneous and viscoelastic. The mechanism of this deformation should be interpreted as structural relaxation oriented by external stress. One can derive a set of simple equations describing the kinetics of homogeneous plastic flow within the framework of such notions.

5:00 PM

Phase Transformations in Metallic Glasses under Pressure: *J. Z. Jiang*[1]; [1]Technical University of Denmark, Dept. of Phys., Bldg. 307, DK-2800 Lyngby Denmark

In this talk, I will present experimental results of crystallization process in metallic glasses under pressure [1]. Several interesting aspects, e.g., crystallization temperature vs. pressure, formation of quasicrystals, time-dependent nucleation process, and TTT diagram, will be addressed. [1] J.Z. Jiang et al, Appl. Phys. Lett. 77, 3553 (2000); N. Wanderka, J.Z. Jiang et al., ibid. 77, (2000) 3935; Y.X. Zhuang, J.Z. Jiang et al., ibid. 77, 4133 (2000); ibid. 79, 743 (2001) ; N. Nishiyama, A. Inoue, and J.Z. Jiang, ibid. 78, 1985 (2001); J.Z. Jiang et al., ibid.79, 1112 (2001); J.Z. Jiang et al., Europhys. Lett. 54, 182 (2001); J.Z. Jiang et al., Phys. Rev. B. (2001) 1st September (in press).

Aluminum Reduction Technology: Inert Anodes

Sponsored by: Light Metals Division, Aluminum Committee
Program Organizers: Martin Segatz, VAW Aluminum AG, D-53117, Bonn Germany; Halvor Kvande, Norsk Hydro ASA, Oslo N-0240 Norway; Wolfgang Schneider, VAW Aluminium AG, Research & Development Manager Cast Technology, Bonn 53177 Germany

Wednesday PM	Room: 6B
February 20, 2002	Location: Washington State Conv. & Trade Center

Session Chair: Les Edwards, CII Carbon, 1615 E. Judge Perez Dr., PO Box 1306, Chalmette, LA 70044 USA

2:00 PM

Inert Anodes: An Update: *R. P. Pawlek*[1]; [1]Technical Info Services & Consulting, Le Forum des Alpes, Ave. du Rothorn 14, CH-3960, Sierre Switzerland

During the last few years the development of inert anodes for the primary aluminium industry has advanced considerably and announcements have influenced the stock market. This update reviews results of tests on (1) anodes made of ferrites (Ni, Co and Zn) alone or in combination with nickel oxide and copper leading to the final composition Ni1-x-yFe2-xMyO4, where M is zinc and/or copper, x is from 0 to 0.5 and y is from 0 to 0.6; (2) anodes made of oxides (Ni, Li, Sn, Sb, Cu) alone or in combinations; and finally (3) anodes made of combinations of metal powders including Ni, Al, Fe, Cu and Zn. The studies examined especially solubility in cryolite alumina melts, but also performance in electrolysis tests from which the results are discussed. Solubility laboratory tests revealed that compositions with limited corrosion (1-2 cm/y) exist and could be successful not only in laboratory but also in industrial cells.

2:25 PM

Electrolysis and Post-Testing of "Inert" Cermet Anodes: *Odd-Arne Lorentsen*[1]; Jomar Thonstad[2]; [1]Norsk Hydro ASA, Rsrch. Ctr., Matls. Dvlp., PO Box 2560, N-3907 Porsgrunn Norway; [2]Norwegian University of Science and Technology, Matls. Tech. & Electrochem., Sem Selandsv. 6, N-7491 Trondheim Norway

Stoichiometric nickel ferrite cermet anodes with 17% copper metal added, making a cermet, were electrolysed for 50 hours in alumina-saturated cryolite-based bath. Bath samples were frequently withdrawn from the cell and analysed with respect to the anode constituents. Steady-state concentrations of iron and copper were below their solubility concentrations, while the nickel concentration was a little higher. Precautions had to be taken to avoid unwanted precipitation of solid alumina and cryolite at the cathode. Post-tests of the anodes showed that copper was depleted in the outer zone of the anode, and the composition of the copper-rich alloy (Cu-Ni-Fe) was changing from the interior toward the surface. However, the metal-depleted surface seemed to be dense, and no voids/pits from the lost metal grains were found in this region.

2:50 PM

The Development of a Metallic Anode and Wettable Cathode Coating and their Tests in a 20-kA Prototype Drained Cell: *Curtis McMinn*[1]; Olivier Crottaz[2]; Vittorio Bellò[2]; Thinh Nguyen[2]; Vittorio de Nora[2]; [1]2125 Chickasaw Dr., Florence, AL 35630 USA; [2]MOLTECH Systems, Ltd., c/o MOLTECH S.A., 9 Rte. de Troinex, Carouge/GE Switzerland

The MOLTECH Group has tested a large range of non-carbon metallic anode materials and designs, modeling the more promising options prior testing them for their retrofittability into drained configuration cells using the required wettable cathode coating developed by MOLTECH and extensively tested in commercial cells of many types. Extensive experience has been gained in design and operating conditions, as MOLTECH has moved to successful testing and operation of a prototype 20-kA cell. This paper will present the results of this research and development work, including a discussion of the experience gained in starting up and operating Non-Carbon Metallic Anodes at the 20-kA cell size, superstructure design issues for retrofitting Hall-Héroult cells into a drained cell configuration, and cell monitoring and control issues. It will conclude with a resume of the status of the cell and anode tests, discussing some of the major problems which have been solved and which are still to be solved.

3:15 PM
Fate of SOFC-Type Inert Anode for Production of Primary Aluminum: *Robert A. Rapp*[1]; Yunshu Zhang[1]; [1]The Ohio State University, Dept. Matls. Sci. & Eng., 2041 College Rd., Columbus, OH 43210 USA

Research supported by the DOE-OIT has evaluated the possibility to use yttria-stabilized zirconia tubes, supplied internally with a metallic anode and fed with reformed natural gas, as an inert anode for retrofit in the Hall-Herault Cell. In principle, electrically-driven titration of oxide ions from alumina-fed cryolite through the oxide-ion conducting electrolyte tubes would lead to a confined anodic reduction site providing significant reductions in cell voltage, cost of production, and release of greenhouse gases. Detailed studies of the solubilities of alumina, zirconia and yttria over a very wide range of cryolite bath ratios (acid-base properties) showed that no bath composition exists where alumina would be sufficiently soluble while the electrolyte components were sufficiently insoluble. Therefore, the SOFC-type anode is not chemically compatible with any cryolite-base solvent system. Solid-state probes were developed which indicated the acid-base state of any cryolite-base melt, and clarified the role of complex anion formation.

3:40 PM Break

3:50 PM
An Alternate Fused Electrolyte/Solvent Suited to the SOFC-Type Anode for Electrowinning Aluminum: *Robert A. Rapp*[1]; [1]The Ohio State University, Dept. Matls. Sci. & Eng., 2041 College Rd., Columbus, OH 43210 USA

In cryolite-base melts, the acid-base range is greatly restricted by the formation of complex oxyfluoride anions. But oxides dissolve in fused sodium sulfate melts to form uncomplexed oxide anions over a wide acid-base range. Extensive previous measurements of oxide solubilities in fused sodium sulfate at 1200K show that in a very basic melt (where NaAlO2 becomes stable) the solubility of alumina is about 10 mol %, while those for zirconia and yttria are very much lower. Therefore, at a temperature suited to the YSZ electrolyte, the chemical conditions required for the SOFC-type inert anode should be satisfied. However, liquid Al is not compatible with fused sodium sulfate, but should react to form a sodium-aluminum sulfide "matte". A preliminary experiment indicated very slow reaction between Al and sodium sulfate, and the YSZ electrolyte is known to support oxide ion titration under such melt conditions. Therefore,the benefits from a SOFC-type inert anode might be realized upon a change in the solvent for alumina to sodium sulfate. Novel modular vertical anode geometries are suggested.

4:15 PM Cancelled
The Corrosion Rate of Cermet Inert Anode with Variety Scale in Aluminum Electrolysis: *Zhao Qun*

Aluminum Sheet and Plate Rolling & Finishing Technology and Applications: Aluminum Rolling-Metallurgy and Microstructure

Sponsored by: Light Metals Division, Aluminum Association,
Program Organizers: Michael H. Skillingberg, The Aluminum Association, Inc., Washington, DC 20006 USA; John P. Brandimarte, Precision Coil, Inc., Clarksburg, WV 26302-2650 USA; Karl Eminger, Alcoa, Inc., Alcoa Mill Products, Lancaster, PA 17604 USA; Seymour G. Epstein, The Aluminum Association, Inc., Washington, DC 20006 USA; Jeff J. Kadilak, Alcan, Inc., Oswego, NY 13126 USA; Leland R. Lorentzen, Nichols Aluminum, Davenport, IA 52801 USA; Douglas N. McLeod, ARCO Aluminum, Inc., Louisville, KY 40242 USA; Ken Schreckengast, Coastal Aluminum Rolling Mills, Inc., Williamsport, PA 17701 USA

Wednesday PM — Room: 608
February 20, 2002 — Location: Washington State Conv. & Trade Center

Session Chairs: J. Daniel Bryant, Alcoa, Inc., Alcoa Technical Ctr., 100 Technical Dr., Alcoa Center, PA 15069-0001 USA; Michael H. Skillingberg, The Aluminum Association, Inc., 900 19th St. N.W., Ste. 300, Washington, DC 20006 USA

2:00 PM
Texture Evolution in Cold Rolled Direct Chill Cast and Continuous Cast Aluminum Alloys: *Wenchang Liu*[1]; Xiyu Wen[1]; Tongguang Zhai[1]; James G. Morris[1]; [1]University of Kentucky, Dept. of Cheml. & Matls. Eng., 177 Anderson Hall, Lexington, KY 40506 USA

The hot bands of direct chill cast (DC) and continuous cast (CC) AA 1100 aluminum alloys were annealed at 399C for 3 hours, and the hot bands of DC and CC AA 5182 aluminum alloys were annealed at 454C for 3 hours. The annealed hot bands were then cold rolled to different reductions. The ODFs of the cold rolled samples were determined by X-ray diffraction in order to compare the texture evolution of DC and CC aluminum alloys during rolling. The texture volume fractions were computed by a new method, in which the Euler space representing all possible crystallographic orientations in rolling was subdivided into the cube, r-cube, Goss, r-Goss, beta fibre, and random orientation regions based on the slip pattern combined with the characteristics of microstructure and texture. Empirical formulas of the texture volume fractions and true strain were constructed to predict the texture in cold rolled aluminum alloys. The effect of the process method (DC vs. CC) and Mg content on the texture after annealing and the texture evolution during the subsequent cold rolling is discussed.

2:25 PM Cancelled
The Evolution of Microstructure and Texture of DC AA3004 Aluminum Alloy through Different Previous Processes of the Hot Band: *Xiangming Cheng*

2:50 PM Cancelled
Microstructure and Local Crystallography of Rolled Al-1%Mn Single Crystals of {001}<110> Orientation: Zhengjie Li

3:15 PM Cancelled
Simulating the Deformation Texture Evolution of Aluminum Alloys during Cold Rolling by using Artificial Neural Network: *Jiantao Liu*

3:40 PM Break

3:55 PM
On the Orientation Hardening and Softening of Strip Cast Sheet of AA5052 Aluminum Alloy during Hot Rolling and Cold Rolling: *Xiyu Wen*[1]; Wenchang Liu[1]; Tongguang Zhai[1]; Jiantao Liu[1]; Xiangming Cheng[1]; J. G. Morris[1]; [1]University of Kentucky, Cheml. & Matls. Eng., 177 Anderson Hall, Lexington, KY 40506 USA

In this paper, an investigation of the work-hardening characteristics of strip cast sheet of AA5052 aluminum alloy during hot rolling and cold rolling is carried out using X-ray crystallographic data. The texture changes during hot rolling and cold rolling reductions were followed by changes in the orientation distribution function (ODF). The orientation hardening and softening caused by a change in the lattice reorientation can lead to either hardening or softening of the matrix, and can be separated from normal dislocation hardening at the grain level. A numerical method is used to derive the rate of orientation hardening and softening and to determine six individual texture components (Cube, Rotated Cube, Goss, Brass, S and Copper components) directly from the ODF data in the alloy sheet. The developments of strain instability during hot rolling and cold rolling are also studied at the grain level. The difference of orientation hardening and softening of the alloy sheet between hot rolling and cold rolling is analyzed and discussed. The significance of orientation hardening and softening on the instability of the sheet metal during hot rolling and cold rolling is also discussed.

4:25 PM
Development of a High Strength Fin Stock Aluminium Alloy: Part II: *Scott W. Haller*[1]; A. Burger[2]; K. Vieregge[2]; A. Haszler[2]; A. Wittebrood[3]; J. van der Hoeven[3]; [1]Corus Aluminum Rolled Products, 9523 Chipping Dr., Richmond, VA 23237 USA; [2]Corus Aluminium Walzprodkte GmbH, Carl-Spaeter-Strasse 10, 56070, Koblenz Germany; [3]Corus Research, Development & Technology, Postbus 10000 (3G16), 1970 CA, IJmuiden The Netherlands

The emphasis in the automotive industry toward heat exchanger units with reduced overall weights and decreased sizes (compact designs) has created a trend for heat exchanger materials with improved performance characteristics. This trend, coupled with the continuous changes in heat exchanger coolants and refrigerants requiring increased system pressure capabilities, has resulted in the development of new materials with higher strengths and improved corrosion resistance characteristics-targeting all components of modern automotive heat exchangers. In order to meet these demands, Corus Aluminium has developed new families of improved alloys for heat exchanger tubes and core plates that are suitable for vacuum and/or controlled atmosphere brazing (CAB). To further complete this development, a program was started to develop a series of high strength alloys for heat exchanger fin applications. This paper presents an overview of the latest laboratory developments and details the plant production trials of the improved Corus Aluminium fin stock alloys.

4:55 PM
A Measurement Capability Study Comparing the Effect of Lubricant Type on Earing of Can Body Stock: *Gary J. Mahon*[1]; Ed Creed[1]; *Jeff J. Kadilak*[2]; [1]Alcan International, Ltd., Banbury Lab., Southam Rd., Banbury, Oxfordshire OX16 2SP UK; [2]Alcan Sheet Products, Oswego Works, PO Box 28, Oswego, NY 13126 USA

The earing test is an important material evaluation technique for sheet products which are to be used in applications where the material will be subjected to a drawing operation. Historically, the most important of these is the draw and re-draw which occurs during manufacture of can bodies. The height of the ears produced during drawing is not only a function of the crystallographic texture of the sheet, but is also strongly affected by the conditions used during the cup drawing operation itself. These include the die clearances, drawing speed, clamping load and surface friction. This paper reports the findings of a statistical study into the reproducibility of the earing test measurements on cups drawn using petroleum jelly as the lubricant (Vaseline) and an industrial grease (Esso Unirex EP2). The study will demonstrate the importance of lubricant type on test reproducibility and the value of the Measurement Capability methodology.

Cast Shop Technology: Grain Refining & Filtration

Sponsored by: Light Metals Division, Aluminum Committee
Program Organizers: David H. DeYoung, Alcoa Technical Center, Alcoa Center, PA 15069 USA; John F. Grandfield, CSIRO Australia, Preston, Victoria 3072 Australia; Wolfgang Schneider, VAW Aluminium AG, Research & Development Manager Cast Technology, Bonn 53177 Germany

Wednesday PM	Room: 6A
February 20, 2002	Location: Washington State Conv. & Trade Center

Session Chairs: Jean-Pierre Martin, Alcan, Arvida Labs. & Dvlp. Ctr., 1955 Mellon Boul., Jonquiere, Quebec G7S 4K8 Canada; Jennifer Black, Vesuvius, PO Box 788, Alfred, NY 14802 USA

2:00 PM Keynote
Grain Refining of Commercial Aluminum Wrought Alloys: *Men Glenn Chu*[1]; [1]Alcoa, Inc., Alcoa Techl. Ctr., 100 Technical Dr., Alcoa Center, PA 15069 USA

Grain refining of aluminum alloys using aluminum-based master alloys containing inoculant particles is practiced daily in most ingot casting plants. The main reasons for grain refining are to reduce ingot cracking during casting and improve ingot fabricability during subsequent thermal mechanical processing. Industrial grain refinement practices are often established based on past experience and not necessarily optimized. Much progress has been made in recent years in the understanding of mechanism of grain refinement and the characteristic of the Al-Ti-B grain refiners. These advances now enable the establishment of grain refining practices for industrial applications based on a scientific basis. In this paper, an overview of current understanding on the mechanism of grain refinement will be presented. The effect of solidification conditions on the effectiveness of grain refiners and the impact of the grain refiner product characteristics on the ingot metal quality will be discussed. The trend of adapting commercial Al-Ti-C grain refiner for critical product applications and recent development of new grain refining techniques including gas-liquid in-situ reaction and acoustic cavitation will also be reviewed.

2:30 PM
A Comparison of Grain Refiner Master Alloys for the Foundry: *D. A. Boot*[1]; P. S. Cooper[1]; D. H. St John[2]; A. K. Dahle[2]; [1]London and Scandinavian Metallurgical Company, Ltd., Aluminium, Fullerton Rd., Rotherham, S. Yorkshire S60 1DL England; [2]University of Queensland, Dept. of Mining, Minls. & Matls. Eng., St Lucia, Queensland QLD 4072 Australia

Grain refiners are widely used in the foundry. They are considered to provide benefits in a number of ways including improved feeding during solidification, reduced and more evenly distributed porosity, and reduced hot tearing. There are a number of refiners for the foundry industry used industrially or mentioned in the literature. A programme of laboratory tests has been carried out, which started with a prescreening of a wide range of potential refiners, using standard laboratory grain refining tests. The better performing refiners were then tested in a permanent mould casting, designed to simulate conditions at the spoke-rim junction of a wheel casting. Results are presented in terms of the effect of refiner on grain size, hot tearing and porosity distribution. Recommendations are made in terms of the optimum refiners for the foundry.

2:55 PM
Investigation on the Grain Refining Behaviors of Al-Ti-C Grain Refiners from Different Suppliers: *Tzu-Hsin Wang*[1]; Kuo-Feng Hsu[1]; Chin-Sheng Chan[1]; [1]China Steel Corporation, Steel & Aluminum R&D, PO Box 47-111, Hsiao Kang, Kaohsiung 81233 Taiwan

From the point of practice it was interesting to know that whether the same type of Al-Ti-C grain refiners from different suppliers provided the same grain refining behaviors or not. The behaviors of commercially available Al-3Ti-0.15C grain refiners from two famous suppliers were investigated using various adding amount, melt temperature and holding time. It was found that the grain refining ability with adding amount of the two grain refiners showed different tendency. Their responses to the aluminum melt temperature were also different. One was sensitive to the melt temperature, the other one was not. One of them showed temperature dependent progressive fading of grain refining ability while held in the melt for a long time, the fading of the other one was not temperature dependent. It was interesting to know that their fading of grain refining ability could not be regained by stirring the melt.

3:20 PM
The Performance of TiB2 and TiC Bearing Grain Refiners in Twin Roll Strip Casting: *Yücel Birol*[1]; Murat Dundar[2]; Selda Ucuncuoglu[1]; Osman Cakir[1]; Abdullah Soner Akkurt[2]; [1]Marmara Research Center, Matls. Technologies, Gebze, Kocaeli 41470 Turkey; [2]Assan Aluminum, Proc. Dvpt., Tuzla, Istanbul Turkey

The master alloys based on the Al-Ti-B system have been used extensively for grain-refining aluminum alloys(1). The TiB2 particles in commercial Al-Ti-B master alloys, however, are rather coarse and have a tendency to agglomerate both during the manufacturing process and after being released into the melt, leading to a number of quality problems. These quality-related problems have created a big demand for an acceptable replacement for Al-Ti-B master alloys. The Al-Ti-C system has thus received particular attention as TiC has been assumed for a long time to be the nucleant for aluminum treated with hypo-peritectic Ti concentrations. TiC particles are claimed to be smaller than the TiB2 particles and are less prone to agglomeration. The Al-3%Ti-0.15%C alloy of this new generation grain refiners have been used commercially for several years in a wide range of alloy systems. Much of the work reported on this alloy, however, has been from laboratory scale testing while data on commercial applications is rather scarce. In the present work, commercially available Al-3%Ti-0.15%C grain refiner was employed in the twin roll strip casting of Al-Fe-Si alloys. Its grain refining potency was compared with that of the Al-5%Ti-1%B master alloy, the standard grain refiner in the aluminum industry.

3:45 PM Break

4:00 PM
The Effects of Rod Grain Refiners with Differing Ti/B Ratio on Ceramic Foam Filtration: *Nicholas Grant Towsey*[1]; Wolfgang Schneider[1]; Hans-Peter Krug[1]; [1]VAW Aluminium AG, Georg-von-Boeselager-Str. 25, Bonn 53117 Germany

The effects of 3%Ti-1%B and 3%Ti-0.15%C rod grain refiners on ceramic foam filtration was previously presented. It was shown that such grain refiners apparently change the filtration behavior leading to lower average filtration efficiencies. The present paper reports the results of follow up investigations into the effects of other grain refiner compositions, viz. 3%Ti-0.2%B, 1.2%Ti-0.5%B and 5%Ti-1%B, on the efficiencies of 50ppi ceramic foam filters. In general terms, it can be said that the new findings tend to support the contention that the alteration of filtration behavior is associated with the boride phase of the Ti-B grain refiners. Together with parallel investigations on relative grain refining potency, an ultimate goal may be to add grain refiner of a certain composition at a lower rate after a ceramic foam filter providing a consistently high quality grain refiner can be supplied. The desired balance may then be realized of optimized ceramic foam filter performance, consistently low inclusion content of metal delivered to the direct chill mould and lowest possible grain refiner costs.

4:25 PM
LiMCA Comparison of a Bed Filter and a Two Stage Ceramic Foam Filter: *D. Corleen Chesonis*[1]; David H. DeYoung[1]; David E. Lake[2]; Neil R. Ridler[2]; [1]Alcoa, Inc., Alcoa Techl. Ctr., 100 Technical Dr., Alcoa Center, PA 15069 USA; [2]Alcoa Manufacturing G.B., Ltd., Waunarlwydd Works, Swansea SA1 1XH Wales

The filtration performance of a bed filter and a two stage ceramic foam filter were compared based on LiMCA inclusion measurements. The bed filter uses a packed bed of alumina mesh and balls to remove inclusions. The two stage filter uses two ceramic foam filter plates; a coarser pore filter is fitted directly over a finer pore filter with a small gap between the two plates. The objective is to use the coarser filter to remove large inclusions so the finer filter can remove more and smaller inclusions without plugging. The main advantage of the two stage filter is to avoid downtime and recovery loss from having to flush the bed filter for alloy changes. LiMCA data was obtained with the bed filter for nine casts and with the two stage filter for five casts. Casts with the two stage filter included three ppi combinations and two filter factors.

4:50 PM Cancelled
Investigation of Inclusion Re-Entrainment during Filtration: *Duygu Kocaefe*

5:15 PM
Metal Quality Analysis at a Continuous Twin Roll Caster: *Edward M. Williams*[1]; Lawrence D. Ray[2]; Tom F. Higdon[3]; [1]Alcoa, Ingot, 100 Technical Dr., Alcoa Center, PA 15069 USA; [2]Alcoa, Flexible Pkgg. R&D, 2101 Reymet Rd., Richmond, VA 23237 USA; [3]Alcoa, Hot Spring Continuous Rolling Plant, Hwy. 270, Jones Mill, AR 72105 USA

LiMCA, Alscan and PoDFA measurements of inclusion and hydrogen concentrations were made at the Hot Springs Continuous Rolling plant casthouse. The purpose of this work was to evaluate the metal quality effects of dramatically reducing and/or eliminating the chlorine used in the in-line degasser. In addition to the reduced chlorine tests, the use of a bonded particle vertical filter, which can be changed in situ during casting, was evaluated. The trial took place at a twin roll continuous caster.

Charles J. McMahon Interfacial Segregation and Embrittlement Symposium: The Effect of Segregation on Environmental Cracking

Sponsored by: ASM International: Materials Science Critical Technology Sector, Structural Materials Division, Materials Processing & Manufacturing Division, Jt. Mechanical Behavior of Materials, Jt. Computational Materials Science & Engineering, Texture & Anisotropy Committee
Program Organizers: Vaclav Vitek, University of Pennsylvania, Department of Materials Science and Engineering, Philadelphia, PA 19104 USA; Clyde Briant, Brown University, Division of Engineering, Providence, RI 02912 USA; Harvey D. Solomon, General Electric Company, Research & Development Center, Schenectady, NY 12309 USA

Wednesday PM	Room: 307-308
February 20, 2002	Location: Washington State Conv. & Trade Center

Session Chairs: Harvey B. Solomon, General Electric, Dept. of Matls. Sci. & Eng., Schenectady, NY USA; David L. Pope, University of Pennsylvania, Dept. of Matls. Sci. & Eng., Philadelphia, PA 19104 USA

2:00 PM Invited
Hydrogen Segregation at Interfaces and its Role in Embrittlement: *Howard K. Birnbaum*[1]; [1]University of Illinois, Matls. Rsrch. Lab., Urbana, IL 61820 USA

Impurity segregation to interfaces generally (but not in every case) has the effect of decreasing the strength of the bonding across that interface and increasing the probability of interfacial fracture. Professor McMahon's research has shown the importance of impurity segregation in determining the mechanical properties and fracture of metals. One important case, that has not been extensively studied is the segregation of hydrogen to interfaces and in particular to grain boundaries. This presentation will review what is known about the segregation of hydrogen to grain boundaries and will relate this segregation to the embrittlement of a number of model systems. The emphasis will be on using the information available to discuss the mechanisms by which hydrogen embrittlement occurs at grain boundaries. It will be shown that hydrogen segregation at grain boundaries plays an important role in at least two mechanisms of hydrogen embrittlement. In one case, Ni–S–H, the synergistic effects of S and hydrogen segregation will be discussed.

2:35 PM Invited
Effects of Grain Boundary Chemistry and Microstructure on the Intergranular Stress Corrosion Cracking of an Al-Mg Alloy: *Russell H. Jones*[1]; Donald R. Baer[1]; Michael J. Danielson[1]; Valery Y. Gertsman[1]; John S. Vetrano[1]; Charles F. Windisch[1]; [1]Pacific Northwest National Laboratory, Matls. Scis., PO Box 999, Richland, WA 99352 USA

Low strength Al-Mg alloys, such as AA5083, are susceptible to intergranular stress corrosion cracking (IGSCC) with thermal aging. Grain boundary chemistry and microstructure measurements have been made using AES and AEM/HRTEM and the role of Mg and Cu on corrosion and stress corrosion measured by XPS and stress corrosion crack growth analysis. Grain boundary enrichment of Mg increases from a ratio of 1.4 to 2.5 upon aging from 1 hr to 100 h at 175C, while grain boundary enrichment of Cu is observed in the solution treated condition and reaches a level of 10 after 100 h at 175C. During this same thermal treatment there is an increase in the volume fraction of the beta phase (Al_3Mg_2) precipitated at grain boundaries. Precipitation proceeds from triple points after 1 h at 175C to more randomly along the grain boundary after 100 h. Corrosion studies of Al implanted with Mg and Cu performed in an XPS system with an in situ corrosion cell showed that both Mg and Cu contribute to the corrosion rate of Al. Increased IGSCC rates occur coincident with these grain boundary microchemistry and microstructure changes. These results will be discussed in terms of anodic dissolution and hydrogen induced crack growth mechanisms for low strength Al-Mg alloys. Research supported by the Office of Basic Energy Sciences of the US Dept. of Energy.

3:10 PM
High Temperature Strength of Two Cryomilled Aluminum Alloys: B. Dehiya[1]; K. Tsuchiya[2]; *J. R. Weertman*[1]; [1]Northwestern University, Matls. Sci. & Eng., Evanston, IL 60208 USA; [2]Toyohashi

University of Technology, Production Sys. Eng., Toyohashi, Achi 441 Japan

Cryomilled aluminum alloys have been found to retain considerable strength at elevated temperatures. Small dispersoids of aluminum oxynitride particles in the tens of nm size range stabilize the microstructure to temperatures approaching the melting temperature. Al-Al2O3 and Al-Al3Ti cryomilled alloys showed little strain hardening and even strain softening, with yield point behavior at elevated temperatures. Strain to failure at elevated temperatures is strain rate sensitive and fracture appears to switch from ductile to intergranular, especially in the Al-alumina material, as the strain rate drops. This research was partially sponsored by Exxon.

3:30 PM Invited
Grain Boundary Segregation and Precipitation on Intergranular Stress Corrosion Cracking of Austenitic Stainless Alloys in High-Temperature Water Environments: *Stephen Michael Bruemmer*[1]; [1]Pacific Northwest National Laboratory, Matls. Interfaces & Characterization, PO Box 999, Richland, WA 99352 USA

Environment-induced intergranular degradation continues to be a critical issue for Fe- and Ni-base stainless alloys in high-temperature water. While the understanding of sensitization has eliminated many problems in oxygenated environments, intergranular stress corrosion cracking remains a common mode of component failure. Grain boundary composition has not been directly linked to degradation in non-sensitized stainless alloys, but considerable new data is available demonstrating complex interactions among segregation, precipitation and environmental cracking. This paper will review and highlight current understanding of grain boundary compositions in Fe- and Ni-base stainless alloys due to both equilibrium and non-equilibrium processes. Beneficial and detrimental segregation of alloying and impurity elements will be discussed along with the influence of second-phase precipitation. High-resolution observations of crack-tip corrosion reactions will be used to illustrate complex effects of local chemistries and precipitate phases on crack advance.

4:05 PM
Analysis of Hydrogen-Induced Decohesion at a Particle/Matrix Interface: *Petros Sofronis*[1]; Yueming Liang[1]; [1]University of Illinois at Urbana-Champaign, Dept. of Theoretl. & Appl. Mech., 216 Talbot Lab., 104 S. Wright St., Urbana, IL 61801 USA

Hydrogen-induced decohesion along grain boundary carbides is a form of material degradation observed experimentally in Ni-base alloys. This decohesion leads to void formation along grain boundaries accompanied by subsequent ductile shearing of the ligaments between voids, thereby causing an intergranular crack to form and propagate. In this paper, the transient hydrogen diffusion around a precipitate is simulated in conjunction with the plastic and elastic deformation correspondingly in the matrix and the particle. The finite element method is used to solve the relevant boundary value problem allowing for decohesion to occur along the particle/matrix interface, and calculate the hydrogen distribution around the precipitate. The thermodynamic theory of Rice and Hirth specialized to the regime of "fast decohesion" is used to describe the interfacial traction-separation constitutive law. The numerical results show that even at small initial hydrogen concentrations, hydrogen can weaken the macroscopic behavior of the material even under "fast decohesion" conditions.

4:25 PM
On the Correlation between Grain Boundary Segregation, Faceting and Embrittlement in Bi Doped Copper: *Wilfried Sigle*[1]; Li-Shin Chang[2]; Wolfgang Gust[1]; Manfred Rühle[1]; [1]Max-Planck-Institut fuer Metallforschung, Seestrasse 92, D-70174 Stuttgart Germany; [2]National Chung-Hsing University, 250, Kuo-Kuang Rd., 402 Taichung Taiwan

Copper Σ19a {331} bicrystals grown by the Bridgman technique have been doped with 14, 25 and 65 at.ppm Bi, respectively. After annealing between 600 and 800°C the segregation was quantified using energy dispersive X-ray spectroscopy in a dedicated scanning transmission electron microscope. Grain boundary faceting on low-index planes was observed and the segregation level was significantly higher at the facets compared to the non-faceted segments. The fraction of faceted grain boundaries was found to increase with increasing annealing temperature implying that the faceting transition is thermally activated. Only the completely faceted grain boundary exhibits brittle behaviour. Faceting appears to be a necessary prerequisite for grain boundary embrittlement of the Σ19a {331} grain boundary by the fact that it allows to incorporated enough Bi atoms. It is suggested that this embrittling mechanism may be a general phenomenon in Bi-doped Cu.

4:45 PM
Corrosion and Stress Corrosion Cracking of Al-Mg Alloys: *Clyde Briant*[1]; Sharvan Kumar[1]; Ping Wang[1]; Zhengfu Wang[1]; [1]Brown University, Div. of Eng., 182 Hope St., Providence, RI 02912 USA

Aging Al-Mg alloys can make them very susceptible to corrosion and stress corrosion cracking because of the precipitation of beta-phase along the grain boundaries. This phase is anodic with respect to the matrix in these alloys and is preferentially corroded. In this paper we examine the effect of small additions of scandium and silver on this intergranular corrosion. Corrosion tests were run by placing the samples in nitric acid for one day and stress corrosion tests were performed by pulling the samples slowly to failure in an NaCl solution. Both sets of tests show that the scandium containing alloy and the alloy that contained neither addition had greater corrosion resistance than the alloys that contained silver. These results are interpreted in terms of the difference in the amount of beta phase precipitated along the grain boundaries.

5:05 PM
On the Stabilization of Grain Boundaries by Solute Segregation: *Reiner Kirchheim*[1]; [1]Universität Göttingen, Inst. für Materialphysik, Hospitalstr. 3-7, Göttingen D-37073 Germany

It will be shown that a certain total area of grain boundaries is in metastable thermodynamic equilibrium in the presence of solute atoms and, therefore, grain coarsening is stopped as there will be no driving force. This is in contradiction to the generally accepted interpretation, where solute drag, i.e. zero mobility of the boundaries stops grain coarsening. Equations for the grain boundary area or the grain diameter, respectively as a function of temperature and solute concentration will be derived based on the excess solute concept of Gibbs. The resulting equations are compared with experimental results. Detailed information about the segregation of phosphorous to grain boundaries in nanocrystalline nickel is obtained from measurements using the tomographic atom probe.

Commercial Mini-Sessions

Sponsored by: Light Metals Division
Program Organizers: David V. Neff, Metaullics Systems Company, Solon, OH 44139 USA; Wolfgang Schneider, VAW Aluminium AG, Research & Development Manager Cast Technology, Bonn 53177 Germany

Wednesday PM	Room: 401
February 20, 2002	Location: Washington State Conv. & Trade Center

Session Chair: David V. Neff, Metaullics Systems Company, 31935 Aurora Rd., Solon, OH 44139 USA

Computational Modeling of Materials, Minerals & Metals Processing: Wednesday PM Plenary Session
2:00 PM – 2:45 PM

Sponsored by: Materials Processing & Manufacturing Division,
Program Organizer: Mark Cross, The University of Greenwich, Centre for Numerical Modelling and Process Analysis, Old Royal Naval College, 30 Park Row, Greenwich, London SE10 9LS UK

Wednesday PM	Room: 619-620
February 20, 2002	Location: Washington State Conv. & Trade Center

Session Chairs: Brian G. Thomas, University of Illinois-Urbana, Dept. of Mechl. & Indl. Eng., Urbana, IL 61801 USA

Keynote
Computational Modeling of Thermo-Mechanical Phenomena: *Christopher Bailey*[1]; [1]University of Greenwich, 30 Park Row, Greenwich, London SE10 9LS UK

Many industrial processes involve materials that are subject to temperature change and thermal stress. Examples range from the casting of large metallic products to the cooling and reliability of small electronic components. Thermally induced stress is a major concern as it can lead to material damage and product failure. Material properties, thermal and mechanical, and process conditions such as the size and location of a feeder in metals casting, or the power dissipation in a computer chip, will govern the magnitude of these stresses. Temperature may also be influenced by fluid flow, for example, the airflow over a computer chip in a laptop will govern the rate of heat extraction, hence the temperature gradients in the chip and the evolving thermal stresses. This paper provides details on the governing equations for heat transfer (temperature) and solid mechanics (stress), their degree of coupling, and the numerical techniques used to solve them. Three examples are discussed to illustrate the use thermomechanical modelling. These also provide an insight into the degree of coupling required between the equations. The first example, involves thermal cycling of electronic components where a prescribed temperature field is applied. As temperature is known, this example only requires the solution of the stress equation. The second example also involves the modelling of an electronic component where the temperature field is also calculated. In both of these examples, the stress calculation is dependent on the temperature field, but the temperature calculation is not dependent of the solution of the stress equation (one-way coupling). The final example provides details on modelling the metals casting process. Both the temperature and stress equations are solved but, unlike the previous two examples, in this case the temperature field is dependent on the results from the stress calculation (two-way coupling).

Computational Modeling of Materials, Minerals & Metals Processing: Thermo-Mechanical Modelling - II

Sponsored by: Materials Processing & Manufacturing Division, *Program Organizer:* Mark Cross, The University of Greenwich, Centre for Numerical Modelling and Process Analysis, Old Royal Naval College, 30 Park Row, Greenwich, London SE10 9LS UK

Wednesday PM — Room: 619
February 20, 2002 — Location: Washington State Conv. & Trade Center

Session Chairs: Chris Bailey, University of Greenwich, 30 Park Row, Greenwich SE10 9LS UK; Brian G. Thomas, University of Illinois-Urbana, Dept. of Mechl. & Indl. Eng., Urbana, IL 61801 USA

2:45 PM
Mathematical Modeling of Mean Flow Stress during Hot Strip Rolling of Nb Microalloyed Steels: *Ki Bong Kang*[1]; Sang Hyun Cho[2]; John J. Jonas[2]; [1]POSCO, Rsrch. Lab., 1 Goedong-dong Nam-gu, Pohang, Kyungbuk 790-785 S. Korea; [2]McGill University, Dept. of Metall. Eng., 3610 University St., Montreal, Quebec H3A 2B2 Canada

The recrystallization behavior of Nb microallyed steels was studied using hot torsion testing with the aim of modeling the recrystallization processes taking place hot rolling. It is shown that the recrystallization kinetics depend on steel composition and processing conditions. The stress-strain curves were determined in order to derive new equations for the peak stress, peak strain, mean flow stress and softening kinetics. The peak strain is influenced by the presence of alloying element; their addition, which has a solute effect, retards the rate of grain boundary motion, shifting the peak to the right. The addition of Ni to the steel results in a significant increment in the activation energy for hot deformation, but Cr has the opposite effect. It was also found that the deformation activation energy in these steels was not altered by the addition of Mo and Nb. The kinetics of static and metadynamic recrystallization were characterized and appropriate expressions were formulated for the recrystallization kinetics. The rate of metadynamic recrystallization increases with strain rate and temperature and is observed to be independent of strain, in contrast to the observation for static recrystallization.

3:10 PM
Modeling of Residual Stresses and Mechanical Behavior of Glass-Infiltrated Spinel Ceramic Composites: *Anil Saigal*[1]; Edwin R. Fuller[2]; Said Jahanmir[2]; [1]Tufts University, Mechl. Eng., 200 College Ave., Medford, MA 02155 USA; [2]National Institute of Standards and Technology, Cer. Div., Bldg. 223, Gaithersburg, MD 20899 USA

All-ceramic crowns, including glass-infiltrated alumina and spinel composites, are coming into widespread use because of their superior aesthetics and chemical inertness. This study investigates the residual stresses that are developed in these composites as a result of cooldown from the glass-infiltration temperature to room temperature due to slight mismatch in the coefficients of thermal expansion and its effect on the mechanical behavior of these composites. Two-dimensional finite element simulations were performed using an object oriented finite element program OOF. The OOF program is a combination of two programs. The first program, PPM2OOF, is designed to read an image file such as a micrograph. The individual pixels that constitute the micrograph may be collected into groups and their material properties assigned. PPM2OOF is then used to create the finite element model/mesh that OOF then reads. The average residual stresses are found to be tensile in the alumina and spinel matrix and compressive in the infiltrated-glass. There is large variation in residual stresses and strains from location to location with presence of locations at which the glass is under tensile stress. The crack initiation and initial propagation in glass-spinel composites is at the glass-spinel interface in both the glass and the spinel. The presence of residual stresses can lead to lower crack initiation stresses and degrade the mechanical properties of the composites.

3:35 PM Break

3:50 PM
Simulation of Fatigue Stress Life (S-N) Diagrams for Ti-6Al-4V Alloy by Application of Artificial Neural Network: S. McShane[1]; *Savko Malinov*[1]; J. J. McKeown[1]; Wei Sha[1]; [1]The Queens University of Belfast, Sch. of Civ. Eng., Belfast, Northern Ireland BT7 1NN UK

A model is developed for prediction of fatigue stress life S-N diagrams for Ti-6Al-4V alloy at different conditions, using Artificial Neural Network (ANN). Different factors which have influence on the S-N diagram are involved as input parameters of the NN, namely microstructure, environment, texture, test/work temperature, surface treatment and stress amplitude. As the output the S-N fatigue diagram is simulated and plotted. The model is based on standard multilayer feed forward neural network. The NN is trained with a comprehensive data set collected from the literature, using Levenberg-Marquardt training algorithm in combination with Bayesian regularisation. A very good performance of the trained Neural Network is achieved. Good correspondence between ANN prediction and experimental S-N diagrams is observed. Using the model S-N diagrams for different conditions are predicted and analysed. Graphical User Interface is developed for use of the model. We believe that the model will be important for practical applications in solving various problems on fatigue behaviour of the titanium alloy.

4:15 PM
Prediction of Lateral and Normal Force-Displacement Curves for Flip-Chip Solder Joints: *Daniel Wheeler*[1]; Daniel Josell[1]; James A. Warren[1]; William E. Wallace[1]; [1]National Institute of Standards and Technology, Metall. Div., 100 Bureau Dr., MS 8555, Gaithersburg, MD 20899-8555 USA

We present the results of experiments and modeling of flip-chip geometry solder joint shapes under shear loading. Modeling, using Surface Evolver, included development of techniques that use an applied vector force (normal and shear loading) as input to determine a vector displacement of the pads connected by the solder joint (standoff height and misalignment). Previous solutions solved the converse problem: fixed displacements used to determine required applied force. Such solutions were inconvenient for applications, where the applied force (chip weight) is known. Also, for geometric and materials studies of solder joint shapes involving multiple parameters, determining the equilibrium displacement from applied force by bracketing solutions could become computationally expensive. Measurements of solder joint standoff height and misalignment as functions of the applied force (normal and shear), solder volume and pad diameter are presented. Experiments were carried out for solder ball diameters from 15 mil (0.029 mm^3 volume) to 6 mil (0.0019 mm^3 volume) on pads of diameter 0.64 mm and 0.35 mm. Fitting of simulation to experimental results gave optimised values for the contact angle and surface tension of the solder which were consistent with measured and literature values.

4:40 PM
Simulation of the Plastic Behavior during Mechanical Testing of Galvanized Steel using the Finite Element Method: *Adriana Salas*[1]; *Martha Patricia Guerrero Mata*[1]; Rafael Colás[1]; René Garza[2]; [1]Universidad Autonoma de Nuevo Leon, FIME-Programa Doctoral en Materiales, Cd. Universitaria, San Nicolas de los Garza, Nuevo Leon 66450 Mexico; [2]Galvak, SA de CV, Quality Assurance, Ave. de la Juventud 340 Nte, Col Cuauhtemoc, San Nicolas de los Garza, Nuevo Leon 66450 Mexico

The use of the finite element method (FEM) for studying the plastic behavior of the metals has become a common practice over the few past years, because it has been proved to be a good means of evaluating processes parameters, and predicting and improving the processes, avoiding the traditional trial and error technique. FEM was used via a commercial package (Ansys) to create a three dimensional model to simulate tension uniaxial simple tests for a galvanized low carbon steel. The aim of the work was to analyze the plastic behavior of a distribution of grains on the zinc cover of a set of galvanized low carbon steel samples. The samples were drawn a mesh with lines 2 mm apart on one of their faces. The samples were deformed at room temperature, at constant low crosshead speed, stopping deformation at different times. Before and during the stops of the testing the deformation measurements were recorded for further calculations in an image analyzer in order to compare these with the computational predictions, as well as validate the numerical model. The results of this study can be extended to other testing conditions, besides the model can used for obtaining constitutive equations.

Computational Phase Transformations: Kinetics of Phase Transformations and Microstructure Evolution

Sponsored by: ASM International: Materials Science Critical Technology Sector, Electronic, Magnetic & Photonic Materials Division, Structural Materials Division, Chemistry & Physics of Materials Committee, Jt. Computational Materials Science & Engineering, Thermodynamics & Phase Equilibria Committee

Program Organizers: Long-Qing Chen, Pennsylvania State University, Materials Science and Engineering Department, University Park, PA 16802-5005 USA; Mark Asta, Northwestern University, Department of Materials Science and Engineering, Evanston, IL 60208-3108 USA; Zi-Kui Liu, Pennsylvania State University, Materials Science and Engineering, University Park, PA 16082-5005 USA; James Aaron Warren, NIST, CTCMS and Metallurgy Division, Gaithersburg, MD 20899-8554 USA

Wednesday PM	Room: 201
February 20, 2002	Location: Washington State Conv. & Trade Center

Session Chair: Duane Johnson, University of Illinois at Urbana-Champaign, Dept. of Matls. Sci. & Eng., 1302 W. Green St., Urbana, IL 61801 USA

2:00 PM
First Principles Computations of Phase Transitions in Oxides and Metals: *Gerbrand Ceder*[1]; Anton Van der Ven[1]; John Reed[1]; [1]MIT, 77 Massachusetts Ave., Rm. 13-5056, Cambridge, MA 02139 USA

First principles energy methods can be used to study the thermodynamics and kinetics of phase transitions in great detail. In ab initio thermodynamics, a system's Hamiltonian is coarse-grained to a model which only contains the most relevant degrees of freedom. In multi-component systems with configurational disorder this leads to a cluster expansion, or generalized Ising Hamiltonian for the energy. The effective interactions in this Hamiltonian can contain the contribution of non-configurational entropy, due to electronic, vibrational or magnetic excitations, and can be easily equilibrated with Monte Carlo Simulation. The methodology for first principles kinetics in alloys is less well established. Besides a correct thermodynamic description, information on the activation energies is now required. In addition, the Monte Carlo method now has to be treated as a kinetic path evolution, rather than as a sampling method. We will present several successful case studies of studying phase transformations and diffusion in transition metal oxides with first principles methods. Several transition metal oxides display reversible and irreversible phase transitions at room temperature. These phase transitions are usually due to a very high mobility of the transition metal ion and/or to the spinodal-like instability in the thermodynamics. High ion mobility can be achieved in oxides through charge disproportionation reactions which allow the ion to obtain its most favorable hybridization at every point along the migration path. This insight has lead to several propositions for engineering the increased stability of these materials. Under some circumstances, chemically embrittled fracture can also be modelled as a phase transition in the appropriate variable space. We show an example of H-embrittlement in metals.

2:30 PM
Ordering Trends in bcc-Based Alloys: *Patrice E.A. Turchi*[1]; Vaclav Drchal[2]; Josef Kudrnowsky[2]; [1]Lawrence Livermore National Laboratory, Chem. & Matls. Sci. Direct. (L-353), PO Box 808, Livermore, CA 94551 USA; [2]Institute of Physics, Acad. of Scis. of the Czech Republic, Na Slovance 2, Praha 8, CZ 182-21 Czech Republic

A majority of the phase diagrams for alloys made of two bcc-based transition metals indicates in the solid phase the existence of a solid solution in the entire range of alloy composition. Using a first-principles electronic-structure approach departures from ideal solid solution behavior are predicted. The methodology is based on the Generalized Perturbation Method applied to the fully relativistic Tight-Binding Linear Muffin-Tin Orbital description of the electronic structure of the chemically random configuration of the alloy. Finite temperature effects are accounted for with the generalized mean-field Cluster Variation Method. Ordering trends and stability properties are rationalized as functions of simple electronic parameters. Work performed under the auspices of the U. S. Department of Energy by the University of California Lawrence Livermore National Laboratory under Contract W-7405-ENG-48.

3:00 PM
Multiscale Modeling of Precipitate Microstructure Evolution: Venu Vaithyanathan[2]; *Christopher Mark Wolverton*[1]; Long-Qing Chen[2]; [1]Ford Motor Company, MD 3028/SRL, PO Box 2053, Dearborn, MI 48121 USA; [2]Pennsylvania State University, Dept. of Matls. Sci., 106 Steidle Bldg., State College, PA 16801 USA

We demonstrate how three "state-of-the-art" techniques may be combined to build a bridge between atomistics and precipitation microstructure: 1) first-principles total energy and linear-response calculations, 2) a mixed-space cluster expansion approach, and 3) diffuse-interface phase-field modeling. The first two methods are used to construct the thermodynamic driving forces for a phase-field microstructural model of θ' Al_2Cu precipitates in Al: bulk free energies, interfacial energies, and elastic strain energies. The incorporation of these energetic properties, obtained from atomistics, into a continuum microstructural model represents a significant step towards predictive modeling of precipitate microstructure evolution.

3:30 PM Break

3:45 PM
Microstructural Evolution in Thermal Gradients: *William C. Johnson*[1]; [1]University of Virginia, Matls. Sci. & Eng., 116 Engineer's Way, PO Box 400745, Charlottesville, VA 22904-4745 USA

Microstructural evolution of thin films on compliant substrates subjected to a temperature gradient through the thickness of the film is examined numerically using Cahn-Hilliard and phase field models. Compositional and transformation strains, strains between the substrate and film, and thermal stresses are considered for a binary alloy which can exist in several different phases. The temperature gradients alter the kinetics of spinodal decomposition, the sequence of phase formation, and the resultant steady-state profiles which evolve with time as compared to isothermal transformations. The effects of substrate material parameters and thickness on evolution are explored. This work is joint with S. Wise, Y. Zhen, P.H. Leo, and is supported by the US Department of Energy through GrantDE-FG02-99ER45771.

4:15 PM
Spinodal Decomposition and Layered Growth in Multiphase Films: *Perry H. Leo*[1]; [1]University of Minnesota, Aeros. Eng. & Mech., 107 Akerman Hall, 110 Union St. S.E., Minneapolis, MN 55455 USA

The microstructural evolution of multiphase films is investigated using a Cahn-Hilliard type equation. The problem is formulated for a binary alloy, and allows for multiple phases, varying temperature, and elasticity. Elastic fields arise from compositional self-strain and thermal mismatch. The governing partial differential equation is solved using a dual-grid finite difference technique that guarantees mass conservation. Results show that quenching the system leads to decomposition at pre-existing interfaces, which may increase the number of layered phases in the system. These extra layers may persist for very long times. Results also show that because of elasticity, the phases that appear may not be equilibrium phases in the absence of elasticity. This work is joint with Y. Zhen, W.C. Johnson and S. Wise, and is supported by the US Department of Energy through Grant DE-FG02-99ER45770.

4:45 PM
Impact of Nucleation Conditions on Transformations: *J. M. Rickman*[1]; [1]Lehigh University, Matls. Sci. & Eng., Bethlehem, PA 18015 USA

We examine quantitatively the impact of various nucleation conditions on the temporal evolution of a phase transformation, with particular emphasis on thin-film systems. Specifically, we characterize the transformation kinetics and resulting microstructures associated with catalyzed nucleation on crystalline defects. This is accomplished via the calculation of non-equilibrium correlation functions, as well as related descriptors of spatial point processes, using both computer simulation and complementary analytical methods. In order to connect our models more closely with experiment, we also discuss image processing strategies that have been employed to interpret relevant TEM micrographs.

5:15 PM
A Phase-Field Model for Coherent Microstructure Evolution in a Thin Film Constrained by a Substrate: Yulan Li[1]; S. Y. Hu[1]; Z. K. Liu[1]; *L. Q. Chen*[1]; [1]Pennsylvania State University, Matls. Sci. & Eng., University Park, PA 16802 USA

A three-dimensional phase-field model has been developed for studying the stability and evolution of coherent microstructure evolution in thin films constrained by a substrate. Elastic solutions are derived for both elastically anisotropic and isotropic thin films with arbitrary domain structures, subject to the mixed surface stress-free and substrate constraint boundary conditions. Electric field in the film is calculated taking into accout the long-range electric dipole-dipole interactions under short-circuit, open-circuit or mixed electric boundary conditions. A specific example of a [001] orientated PbTiO3 film heteroepitaxially grown on a [001] cubic substrate is considered. We investigated the effect of substrate constraint, temperature and depolarization on the volume fractions of ferroelectric domain variants, domain-wall orientations, surface topology, domain shapes, and their temporal evolution for a cubic-to-tetragonal ferroelectric phase transition. It is shown that the shapes of a-domains with tetragonal axes parallel to the film surface are significantly different from those of c-domains with tetragonal axes perpendicular to the film surface. For the substrate constraints and temperatures under which both a1- and a2-domains coexist, both types of a-domains are present with their tetragonal axes perpendicular to each other, and the domain wall orientations deviate from the 45 degree orientation generally assumed in thermodynamic analyses. It is demonstrated that a substrate constraint results in sequential nucleation and growth of different tetragonal domains during a ferroelectric phase transition. The effect of depolarization on the domain shape and domain variant volume fraction will be discussed.

Creep Deformation: Fundamentals and Applications: High Temperature and Advanced Materials

Sponsored by: ASM International: Materials Science Critical Technology Sector, Structural Materials Division, Materials Processing & Manufacturing Division, Jt. Mechanical Behavior of Materials, Powder Materials Committee
Program Organizers: Rajiv S. Mishra, University of Missouri, Metallurgical Engineering, Rolla, MO 65409-0340 USA; James C. Earthman, University of California, Department of Chemical and Materials Science, Irvine, CA 92697-2575 USA; Sai V. Raj, NASA Glenn Research Center at Lewis Fields, Cleveland, OH 44135 USA

Wednesday PM	Room: 214
February 20, 2002	Location: Washington State Conv. & Trade Center

Session Chair: J. D. Whittenberger, NASA-Glenn Research Center, Matls. Div., MS 24-1, 21000 Brookpark Rd., Cleveland, OH 44135 USA

2:00 PM Invited
Microstructure and Creep Strength of Fourth Generation Single Crystal Superalloys: *Hiroshi Harada*[1]; [1]National Institute for Materials Science, High Temp. Matls. Rsrch. Grp., 1-2-1 Sengen, Tsukuba Science City, Ibaraki 305-0047 Japan

Fourth generation single crystal(SC) Ni-base superalloys with plutinum group metals additions have been developed along the guidelines given by our alloy design computer programs. In the present paper, the relationship between microstructures and creep properties of the alloys are examined and compared with their mother alloy TMS-75, our third generation SC superalloy. The role of larger negative lattice misfit as well as microstructural stability will be discussed for understanding the excellent creep resistance at higher temperature and lower stress creep conditions, e.g., over 400h rupture life at 1100C/137MPa, with the developed fourth generation SC superalloys.

2:25 PM
Effect of Microstructure on Creep in Directionally Solidified Eutectic NiAl-31Cr-3Mo: *J. Daniel Whittenberger*[1]; S. V. Raj[1]; [1]NASA-Glenn Research Center, Matls. Div., MS 24-1, 21000 Brookpark Rd., Cleveland, OH 44135 USA

Directional solidification of eutectic NiAl-31Cr-3Mo (at. %) can yield a combination of reasonable room temperature toughness (~20 MPa√m) and good creep strength (~100 MPa at 1300 K and 10^{-7} s^{-1}) which makes this material attractive for use in elevated temperature, oxidizing environment conditions. The 1200-1400 K deformation properties of as-cast NiAl-31Cr-3Mo and alloy rods directionally solidified at growth rates between 7.6 to 508 mm/h have been characterized in compression at strain rates ranging from 10^{-3} to 10^{-9} s^{-1}. In addition extensive light optical microstructural analysis of the directionally solidified NiAl-31Cr-3Mo has been undertaken to determine the average spacing, cell size, intercellular region thickness, etc. This presentation will focus on correlations between microstructure and creep properties and the connection of microstructure with the underlying mechanisms controlling deformation in this eutectic.

2:45 PM
Microstructure Design Near Grain Boundaries for Creep Resistant Tempered-Martensitic 9Cr Steels for 650°C USC Boilers: *F. Abe*[1]; T. Horiuchi[1]; M. Taneike[1]; K. Kimura[1]; S. Muneki[1]; H. Okada[1]; [1]National Institute for Materials Science Japan

National Institute for Materials Science (formerly, National Research Institute for Metals) has been conducting the research and development of advanced ferritic steels for application to thick section boiler components of ultra-supercritical (USC) power plant at 650°C.The project involves the improvement of creep strength, oxidation resistance and creep-fatigue properties for high-Cr ferritic steels, including welded joints. This paper describes the microstructure design near grain boundaries for the improvement of long-term creep strength at 650°C. A tempered-martensitic steel ASME T91 (9Cr-1MoVNb steel) exhibits a rapid decrease in creep strength at long times above 10,000 h at 600 to 650°C. The TEM observations show that preferential recovery of lath martensitic microstructure proceeds in the vicinity of prior-austenite grain boundaries at low stresses and long times above 10,000 h, involving agglomeration of carbonitrides and coarsening of lath near grain boundaries. The preferential recove ry of microstructure causes the transition from the primary or transient creep to the tertiary or acceleration creep at shorter times, which results in higher minimum creep rate and shorter creep life. Suppression of preferential recovery of lath martensitic microstructure near grain boundaries has been examined by optimizing the distributions of precipitates for a tempered-martensitic 9Cr-3WVNb steel and for a carbon-free martensitic Fe-12Ni-9Co-10W-0.2Ti-0.1Al alloy which is a modification of low-carbon maraging steel.Homogeneous dispersion of fine M23C6 carbides at lath boundaries has been achieved for up to long times for the 9Cr-3WVNb steel with small amount of boron. This results in stabilization of lath martensitic microstructure near grain boundaries and hence improves long-term creep strength. The enrichment of boron into M23C6 carbides becomes more significant with reaching prior-austenite grain boundaries. Homogeneous dispersion of fine V(Nb)-nitrides and intermetallic compounds at lath boundaries as well as within lath near grain boundaries has been also obtained for the 9Cr-3WVNb steel with minimized carbon and the Fe-12Ni-9Co-10W-0.2Ti-0.1Al alloy, respectively. Based on the experimental results, the optimization of microstructure near grain boundaries will be described.

3:05 PM
Creep Behavior of Binary NiAl: *S. V. Raj*[1]; [1]NASA Glenn Research Center, Matls. Div., MS 24-1, 21000 Brookpark Rd., Cleveland, OH 44135 USA

Constant load creep tests were conducted on binary NiAl. Two types of primary creep transients were observed depending on stress and temperature. First, at low temperatures and stresses, there was an initial sharp decrease in the creep rate soon after the application of the applied stress followed by inverse primary creep, where the creep rate approached a steady-state value. Second, at high temperatures and stresses, normal primary creep was observed after the specimen was loaded. These observations suggest that primary creep in binary NiAl is limited by dislocation mobility. Power-law creep with a stress exponent of about 6 and activation energy of about 300 kJ/mol was observed between 1000-1300 K. At stresses below 25 MPa, a new mechanism was observed with a stress exponent of about 2 and an activation energy of about 100 kJ/mol. This mechanism was observed to be grain size dependent.

3:25 PM
Creep Behavior at 1050°C of a New Generation Single Crystal Superalloy: *Frédéric Diologent*[1]; Pierre Caron[1]; Alain Jacques[2]; Pierre Bastie[3]; [1]Onera, DMMP, 29 Av de la Division Leclerc, Châtillon 92322 France; [2]LPM, UMR 7556, Ecole des Mines de Nancy, Parc de

Saurupt, Nancy 54042 France; [3]LSP, UMR 5588, Université Joseph Fourier, Saint-Martin-d'Hères 38402 France

We have compared the creep behavior at 1050°C of two nickel-based single crystal superalloys: the first generation AM1 alloy and the new generation MC-NG alloy containing rhenium and ruthenium and showing a very high creep strength at elevated temperatures. The creep life of MC-NG was longer than that of AM1, but both alloys did not show similar creep behavior. The creep stages of each alloy were analyzed to understand this discrepancy. Attention was focused on the evolution of the γ/γ' lamellar microstructure during the creep deformation. The determination of γ/γ' lattice mismatches in creep-deformed MC-NG suggests that the microstructural evolution, and therefore the creep behavior, is related to the variation in the difference of lattice mismatch between the horizontal and vertical γ/γ' interfaces. The analysis of the dislocation structures evidenced some differences between the two alloys which could contribute to the creep behavior modifications.

3:45 PM Break

3:55 PM

Creep Behavior and TEM Observation of the First and Third Generation Ni-base Single Crystal Superalloys: *Takao Murakumo*[1]; Toshiharu Kobayashi[1]; Shizuo Nakazawa[1]; Yutaka Koizumi[1]; Hiroshi Harada[1]; [1]National Institute for Materials Science Japan, High Temp. Matls. Rsrch. Grp., 1-2-1 Sengen, Tsukuba Science City, Ibaraki 305-0047 Japan

Ni-based single crystal superalloy has been developed by Re addition. Actually, the creep rupture life of a first generation SC superalloy TMS-26 is shorter than that of TMS-75, a third generation Ni-base SC superalloy at 900°C/392MPa. However, the steady state creep region and rupture life of TMS-26 are indeed longer than those of TMS-75 at 1100°C/137MPa. In this study, we observe microstructures with TEM, and differences in creep mechanism are discussed. At lower temperature and higher stress, it is effective to delay rafting for extending creep rupture life. On the other hand, at higher temperature and lower stress, it is expected that rupture life becomes longer when raft structure is stable. In the case of this study, all of factors benefit TMS-26 for rafting rather than TMS-75, resulting in better creep strength at 1100°C/137MPa and shorter creep life at 900°C/392MPa.

4:15 PM

On the Influence of Shear Loading Direction on the Creep Response of Super Alloy Single Crystals: *Kazim Serin*[1]; Muthuswamy Kamaraj[2]; Matthias Kolbe[3]; Gunther Eggeler[1]; [1]Ruhr-Universitat-Bochum, Inst. for Matls., Universitatsstr. 150, Bochum 44780 Germany; [2]Indian Institute of Technology, Dept. of Metlgcl. Eng., Madras 600036 India; [3]DLR, Inst. for Space Simulation, Koln 51170 Germany

Recently a shear creep test technique for superalloy single crystals was developed which can be used at temperatures up to 1100°C [1]. This technique allows to load specific macroscopic crystallographic slip systems. So far the test technique was used to study microstructural processes associated with high temperature and low stress creep [e.g. 2,3]. In the present paper we report a complete set of shear creep data for the super alloy single crystal material CMSX4. Constant stress tests are performed on four macroscopic crystallographic slip systems. We discuss the shape of individual creep curves as well as the stress and the temperature dependence of the secondary creep rate. In addition an attempt was made to study the influence of a change of load direction. One specimen was shear loaded on the {111} plane in <01-1> direction until a shear strain of 6.5% was reached. Then the test was interrupted and continued in <0-11> direction. After this change creep rates were observed to be ten times higher than bef ore. This result is discussed on the basis of the underlying dislocation processes which govern high temperature and low stress creep. [1] C.Mayr, G.Eggeler, G.A.Webster, G.Peter, Mat. Sci. Eng., A199 (1995) pp. 121-130; [2] M.Kamaraj, C.Mayr, M.Kolbe, G.Eggeler, Scripta Mater., 38 (1998) pp. 589-594; [3] G.Eggeler, A.Dlouhy, Acta Mater., 45 (1997) pp. 4251-4262.

4:35 PM

Structure and High-Temperature Mechanical Behavior Relationship in Nano-Scaled Multilayered Materials: *Nathan Allan Mara*[1]; Alla Sergueeva[1]; Amiya K. Mukherjee[1]; [1]University of California-Davis, Cheml. Eng. & Matls. Sci., One Shields Ave., Davis, CA 95616 USA

Nanometer-scale polycrystalline multilayered films (layer thickness less than 100 nm) have been the subject of many recent experimental and theoretical studies. These fine-scale composite materials typically exhibit high yield strength, often approaching the theoretical strength at room temperature. Most attempts to characterize the mechanical behavior of such thin films have been carried out using nanoindentation and scanning force microscopy or their combination and there is little data regarding their mechanical behavior at elevated temperatures. In the present investigation, the microstructure and mechanical properties of polycrystalline Cu-Nb nanolayered composites prepared by magnetron sputtering and electrodeposited Cu-Ni nanolayered composites were evaluated. Samples were tested in uniaxial tension at temperatures ranging from 25 to 550°C at different strain rates. The high strength of these new materials is attributed to their layered, nanoscale structure and a variety of related strengthening m echanisms. This investigation is supported by NSF, Division of Materials Research, grant NSF-DMR-9903321.

4:55 PM

Characterization of Key Modeling Parameters in the Modified Jogged-Screw Model for Creep of Equiaxed Gamma TiAl: *Karthikeyan Subramanian*[1]; Gopal B. Viswanathan[1]; Michael J. Mills[1]; [1]The Ohio State University, Dept. of Matls. Sci. & Eng., 2041 College Rd., Columbus, OH 43210 USA

Transmission Electron Microscopy studies on crept samples of an equiaxed Ti-48Al alloy deformed to strains near the minimum strain rate show a microstructure dominated by unit 1/2[110] type dislocations. These dislocations are pinned by jogs of varying heights. The jogged-screw model is adopted, where the rate controlling step is assumed to be the non-conservative dragging of the jogs along the length of the screw dislocations. The presence of tall jogs and the existence of a stress-dependent upper bound to the height of tall jogs which can be dragged have been incorporated into the model. These modifications lead to excellent agreement with experimental data. Simulation of the movement of these jogged-screw segments have lead to the identification of the key microstructural parameters that control the creep rate. Attempt has been made to characterize these modeling parameters as a function of stress, strain and temperature. The evolution of the creep curve is also qualitatively predicted.

5:15 PM Discussion Session

Deformation and Stresses in Small Volumes: Deformation Mechanisms

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

Program Organizers: David F. Bahr, Washington State University, Department of Mechanical & Materials Engineering, Pullman, WA 99164-2920 USA; Eric Kvam, Purdue University, School of Materials Engineering, West Lafayette, IN 47907-1289 USA; Scott X. Mao, University of Pittsburgh, Department of Mechanical Engineering, Pittsburgh, PA 15261 USA; Neville R. Moody, Sandia National Laboratories, Livermore, CA 94551-0969 USA

Wednesday PM	Room: 303
February 20, 2002	Location: Washington State Conv. & Trade Center

Session Chair: Scott Mao, University of Pittsburgh, Mechl. Eng., 3700 O'Hara St., Pittsburgh, PA 15261 USA

2:00 PM Invited

TEM Investigation of Nanoindentation Induced Deformation Structures in W/NbN Nanolaminates: *Michael F. Savage*[1]; Donald K. Kramer[1]; Aric Lin[1]; Tim Foecke[1]; Scott A. Barnett[2]; [1]National Institute of Standards and Technology, Metall. Div., 100 Bureau Dr., MS 8553, Gaithersburg, MD 20899 USA; [2]Northwestern University, Matls. Sci. & Eng., Evanston, IL 60208 USA

Understanding the deformation mechanisms in nanolaminated composites is an important step towards developing constitutive laws that describe their mechanical behavior. Several mechanisms have been proposed, however experimental corroboration is difficult due to the small length scales associated with these materials and limited means of mechanical testing. The nanoindentation test is an attractive choice as a mechanical probe due to the ease of sample preparation and available analysis procedures. The measure of a material's resistance to plastic deformation, the hardness, is often related to yield strength through Tabor's relationship, in which hardness is three times the yield stress, or according to Johnson's spherical cavity model. However, these models assume that the material is a homogeneous isotropic solid. Their applicability to nanolaminated composites is unknown. In this study, the deformation mechanisms in single crystal tungsten and epitaxial W/NbN superlattices with bilayer spacings from 5 nm to 30 nm are investigated by means of a novel indentation technique. Cross-section transmission electron microscopy is then used to study the deformation mechanisms, and compare the size and shape of the plastic zones underneath the contact. Differences within the range of bilayer spacings and between the superlattices and tungsten single crystal will be discussed.

2:30 PM

Quantitative In Situ Nanoindentation of Thin Films: *Andrew M. Minor*[1]; Eric A. Stach[2]; J. W. Morris[1]; [1]University of California-Berkeley and Lawrence Berkeley National Laboratory, Dept. of Matls. Sci. & Matls. Sci. Div., One Cyclotron Rd., MS 66-200, Berkeley, CA 94720 USA; [2]Lawrence Berkeley National Laboratory, Natl. Ctr. for Electron Microscopy, One Cyclotron Rd., MS 72, Berkeley, CA 94720 USA

The fundamental processes that initiate deformation can be measured and observed directly through a nanoindentation experiment. Typically, these discrete microstructural events are examined ex situ, and ex post facto, in which important details may be missed or lost. Recently, we have developed a method for quantitative, in situ nanoindentation in an electron microscope. The initial application of this new technique will be presented, in which we have studied the onset of deformation during the nanoindentation of aluminum and other metallic thin films. The force-displacement curve developed shows the characteristic "staircase" instability at the onset of plastic deformation. This instability corresponds to the first appearance of dislocations in a previously defect-free grain. These results represent the first real time measurements and observations of the discrete microstructural events that occur during nanoindentation.

2:50 PM

Dislocation Emission and Subsequent Interactions with Sigma = 3 Boundaries in Epitaxial Au Thin Films: *Gene A. Lucadamo*[1]; Douglas L. Medlin[1]; [1]Sandia National Laboratories, Thin Film & Interface Sci., MS 9161, PO Box 969, Livermore, CA 94551-0969 USA

We report on the origin and nature of dislocation arrays formed near facet junctions in (111) Au thin film bicrystals. Using room temperature and in situ hot stage transmission electron microscopy (TEM), we have studied dislocations at the junctions between orthogonal $\Sigma=3$ {111} and $\Sigma=3$ {112} faceted grain boundaries. Dislocation arrays were observed with b=1/6<112> in {111} twin boundaries near {112} facet junctions. Experiments conducted in the TEM at elevated temperature showed that the arrays originated from the emission of secondary grain boundary dislocations (SGBDs) and that the motion of the emitted dislocations was coupled with the migration of the {112} facet junctions. The SGBDs accommodated a rotational misorientation between adjacent crystallographic domains. This interpretation was corroborated by measurements showing that the domains in the vicinity of the facet junctions deviated slightly (<1°) from the exact $\Sigma=3$ coincident-site-lattice (CSL) orientation. We propose that the driving forces for this motion are provided primarily by the climb stress between the SGBDs arising from the discontinuous character of the {112} boundary at the intersection with the horizontal twin plane. This work was partially supported by the US Department of Energy, Office of Basic Energy Sciences, under contract number DE-AC04-94-AL85000.

3:10 PM

Deformation of Small Volumes of Material Studied using Strained Layer Superlattice Structures: *Andrew J. Bushby*[1]; David J. Dunstan[2]; Patricia Kidd[3]; Anthony Kelly[4]; [1]Queen Mary, University of London, Dept. of Matls., Mile End Rd., London E1 4NS UK; [2]Queen Mary, University of London, Dept. of Phys., Mile End Rd., London E1 4NS UK; [3]Philips Analytical Research Centre, Cross Oak Ln., Redhill RH1 5HA UK; [4]University of Cambridge, Dept. Matls. Sci. & Metall., Pembroke St., Cambridge CB2 3QZ UK

Mechanical studies of semiconductor superlattices have shown that the onset of plastic deformation under an inhomogeneous stress is a process that takes place simultaneously across a finite volume of the order of a micron across. The deformation behaviour of materials under contact loading is of prime technological importance, and a criterion for yielding is important as a design tool. As technology moves increasingly to smaller scales in thin film coatings, nanostructured materials and micro-electro-mechanical systems, existing yield criteria fail rather badly. The ability to incorporate known internal stresses, and to vary the stress and thickness of individual layers in a semiconductor superlattice, is a very powerful tool, opening up new possibilities for investigations that cannot be achieved by varying external stresses on a specimen that is sensibly homogeneous. In this way, from the initial yield stress of single-crystal strained-layer superlattices under indentation, we demonstrate a new criterion, of which the key feature is that it is to be averaged over a finite volume. By careful design of the superlattice stress in individual layers, the size and position of the initial yield volume can be determined and the yield criteria deduced.

3:30 PM Break

4:00 PM

Heteroepitaxial Aluminum Thin Films on Silicon: A Model System for Understanding Thin Film Plasticity: *Eric A. Stach*[1]; Karla Balzuweit[1]; Ulrich Dahmen[1]; David Nowak[2]; Shefford P. Baker[2]; [1]Lawrence Berkeley National Laboratory, Natl. Ctr. for Electron Microscopy, MS 72-150, Berkeley, CA 94720 USA; [2]Cornell University, Dept. of Matl. Scis. & Eng., 214 Bard Hall, Ithaca, NY 14853 USA

Through careful choice of substrate orientation and deposition temperatures, it is possible to grow aluminum heteroepitaxially on silicon. In particular, single crystal, bi-crystal and tri-crystal geometries have been demonstrated. Because of the orientation relationships established, it becomes possible to determine the resolved shear stresses on particular slip systems during thermal cycling. In prior work, we have used in-situ transmission electron microscopy to determine how dislocations mediate plastic deformation during cooling from elevated temperatures in bicrystalline films. Dislocations are introduced into the film by nucleation at grain boundary cusps. These events occur in ensembles at particular temperatures, where resolved shear stresses are on individual dislocations are on the order of 300 to 350 MPa. Herein, we correlate these observations with x-ray microdiffraction studies of strain relaxation and extend these studies to single and tri-crystal microstructures. Direct comparison of these observations with polycrystalline films will be presented, allowing insight into the general behavior of dislocations in thin metal films.

4:20 PM

N-Edge Dislocations in Thin Bent Foils and N-Screw Dislocations in Circular: *Johannes Weertman*[1]; [1]Northwestern University, Dept. of Matls. Sci. & Eng., 2225 N. Campus Dr., Evanston, IL 60208 USA

Anomalous hardening was observed by Stölken and Evans in thin bent nickle foils and by Fleck, Muller, Ashby and Hutchinson in twisted copper rods of small diameter. The anomalous hardening has been explained as a caused by the presence of N_dislocations. (Here 'N' stands for geometrically necessary or non-redundant dislocations and 'R' stands for redundant or statistically stored dislocations.) Stölken and Evans attribute the anomalous hardening in bent foils to N-edge dislocations. They assume that the flow stress is proportional to the square root of the sum of the R-dislocation density and the N-dislocation density. Anomalous hardening occurs when the latter density is greater than the former. Fleck and Hutchinson have the same explanation and ascribe the anomalous hardening in torsion rods to N-screw dislocations that are oriented parallel to the axis of the torsion specimen. Hurtado and Weertman analyzed anomalous hardening with N-screw dislocations that lie in the planes perpendicular to the torsion axis. However, they disagree that the anomalous hardening is simply the result of swamping of the total dislocation density by N-dislocations (because insufficient R-dislocation exist to pin N-dislocations). We will show in this talk it is not possible for the anomalous hardening in torsion to arise from twist boundaries formed by combining N-screw dislocations that are parallel to and N-screw dislocations that are perpendicular to the specimen axis because the sign of the N-screw dislocations in one set of dislocations is opposite that of the other. If they could have formed the case for hardening by N-dislocation swamping would be strengthened. The N-screw dislocations all move in the same radial directions (towards the center of the torsion bar) and are not likely to hinder each others motion significantly. The central theme of this talk is that N-dislocation density swamping is not needed for anomalous hardening. The imposition of the condition that the N-dislocation density is less than or equal to the R-dislocation density everywhere in a sample leads to anomalous hardening (by reducing the N-dislocation density and the amount of plastic deformation produced at a given stress level). That this N-dislocation skimping condition does so is shown explicitly in detail for the problem of the thin bent foil.

4:40 PM

Stress Effects in SiO2 Thin Films: *Terry J. Delph*[1]; Ralph J. Jaccodine[1]; Ming-Tzer Lin[1]; [1]Lehigh University, Mechl. Eng. & Mech., 19 Memorial Dr. W., Bethlehem, PA 18015 USA

Stress effects on the oxidation of silicon become of considerable importance in the design of sub-micron structures, where many instances of anomalous oxide thinning have been observed. We describe the state of the art in modeling these stresses. We further report upon recent work upon the oxidation of planar silicon substrates. Oxidation of planar substrates can result in substantial levels of compressive stress. Experimental results from oxidizing substrates tested in bending implicate the substrate strain as one of the factors influencing the thinning behavior.

Fatigue and Creep of Metal Matrix Composites: Creep of Metal Matrix Composites

Sponsored by: Structural Materials Division, Jt. Composite Materials Committee
Program Organizers: Nikhilesh Chawla, Arizona State University, Department of Chemical and Materials Engineering, Materials Science and Engineering Program, Tempe, AZ 85287-6006 USA; John J. Lewandowski, Case Western Reserve University, Department of Materials Science and Engineering, Cleveland, OH 44106 USA

Wednesday PM	Room: 206
February 20, 2002	Location: Washington State Conv. & Trade Center

Session Chairs: Efrain Carreño-Morelli, University of Applied Sciences of Western Switzerland, Competence Grp. Matls. & Design, Rte. de Rawyl 47., Sion CH-1950 Switzerland; David C. Dunand, Northwestern University, Dept. of Matls. Sci. & Eng., Evanston, IL 60208 USA

2:00 PM Keynote
Creep Behavior of Metal Matrix Composites: A Comparison with Pure Metals and Alloys: *Terence G. Langdon*[1]; [1]University of Southern California, Depts. of Aeros. & Mechl. Eng. & Matl. Sci., Los Angeles, CA 90089-1453 USA

There are important differences between the creep behavior of metal matrix composites and unreinforced pure metals and metallic alloys. This paper examines these differences and develops procedures for data analysis.

2:40 PM Invited
Creep Cavitation in Aluminum Containing High Volume Fractions of Alumina Dispersoids: Bing Q. Han[1]; *David C. Dunand*[2]; [1]University of California, Dept. of Mechl. & Aeros. Eng., Irvine, CA 92717-3975 USA; [2]Northwestern University, Dept. of Matls. Sci. & Eng., Evanston, IL 60208 USA

Density measurements were used to quantify creep cavitation in pure aluminum containing very high volume fractions (25-42 vol.%) of alumina dispersoids with a mean diameter of 280 nm. In the range of creep temperatures studied (370-450°C), the cavity fraction increases linearly with strain, i.e. the ratio of cavity fraction to strain is constant. This cavitation ratio (i) decreases with increasing stress at constant temperature; (ii) is weakly dependent on temperature at constant stress; (iii) increases with increasing volume fraction of dispersoids at constant stress and temperature; (iv) is independent of matrix grain size. The latter result indicates that cavitation occurs at dispersoid/matrix interfaces, not at matrix grain boundaries. Results are compared to existing creep cavitation models in pure metals and metal matrix composites.

3:10 PM
Creep Deformation and Rupture Behavior of Laminated Metal Matrix Composites: *S. B. Biner*[1]; [1]Ames Laboratory, Iowa State Univ., 208 Metals Dvlp., Ames, IA 50011 USA

In this study, the creep behavior at 250 Co of laminated composite consists of 6061-Al alloy layers and 2014-Al-20vol%SiC particulate reinforced composite layers was investigated. In spite of the absence of delamination between the layers, the observed creep rupture times of the laminated composite were much shorter than those seen for its constituent phases. This behavior is explained with a model based on the laminate theory. This work was performed for the United States Department of Energy by Iowa State University under contract W-7405-Eng-82.

3:30 PM Break

3:50 PM Invited
Creep Behavior of Composite Lead-Free Electronic Solder Joints: *K. N. Subramanian*[1]; [1]Michigan State University, Dept. Cheml. Eng. & Matls. Sci., E. Lansing, MI 48824-1226 USA

Electronic solders used in surface mount technology need to be reasonably strong to maintain the structural integrity, and should also be reasonably compliant to avoid component failures by the stresses that develop due to CTE mismatches during thermal excursions experienced in service. Service life of such solder joints depend not only on the steady state creep-rate but also on the strain for onset of tertiary creep. Roles of compatible intermetallic reinforcements introduced into lead-free Sn-Ag solders by either in-situ or mechanical means on both secondary creep-rate and strain for onset of tertiary creep will be discussed. Composite approach to increase the solder joint service life will be evaluated on the basis of time duration spent in steady state creep condition as a function of stress and temperature. Acknowledgment: Project funded by Composite Materials and Structures Center at Michigan State University.

4:20 PM
Advances in the Use of Neutron Diffraction to Study Strain Partitioning in Composites: *Mark A. Bourke*[1]; David C. Dunand[2]; Ersan Üstündag[3]; [1]Los Alamos National Laboratory, MST, MS H805, Los Alamos, NM 87545 USA; [2]Northwestern University, Dept. of Matls. Sci. & Eng., 1083 MLSB, 2225 N. Campus Dr., Evanston, IL 60208-3108 USA; [3]California Institute of Technology, Dept. of Matls. Sci., 309 Keck Laboratory, MC 138-78, 1200 E. California Blvd., Pasadena, CA 91125 USA

In the summer of 2001, a load frame-furnace suite will be implemented at Los Alamos National Laboratory on a new neutron scattering spectrometer called the Spectrometer for Materials Research at Temperature and Stress (SMARTS). The value of neutron diffraction for studying mechanical strain response in multi-phase polycrystalline systems is that it can resolve phase-specific strain, averaged over a volume representative of the bulk response. Thus by recording diffracted spectra during loading of e.g. a metal/ceramic composite, the elastic strain in the metal matrix can be distinguished from the strain in the ceramic reinforcement. At elevated temperature, creep in the metal alters the composite load partitioning which is reflected in changes to the lattice strain. The new system is noteworthy by virtue of its uniaxial 250KN/1500°C load-temperature capacity under vacuum or controlled atmosphere. This talk will illustrate the capabilities by example. Some systems that are planned for investigation in 2001 include Al-Al_2O_3, Ti-SiC, SiC-Si_3N_4, WC-Co and Waspaloy.

4:40 PM
High Strain Rate Superplasticity of TiN and TiB2 Particulates: *Tsunemichi Imai*[1]; Liang Zhen[2]; Makoto Takagi[3]; [1]National Institute of Advanced Industrial Science and Technology Japan; [2]Harbin Institute of Technology China; [3]Aichi Institute of Technology Japan

TiN and TiB2 particulate reinforced aluminum composites fabricated by powder metallurgical method were extrued and hot-rolled to build fine microstructures and effect of aluminum alloy matrix on the high strain rate superplasticity (HSRS) was investigated. TiN/2014 Al composite exhibits the m value of 0.30~0.43 in the temperature of 773~818K and in the strain rate range higher than 10-1s-1 and maximum total elongation of 370% at the strain rate of 3x10-1s-1 and at 818K, although TiN/2017 Al indicates about 200% at the strain rate of 3x10-2 ~ 3x10-1s-1 and at 818K. And TiN/1N90 pure Al could produce about 200% elongation at the strain rate of 2x10-1s-1 and at 923K. But TiN/Al-1Mg could not produce large elongation. On the other hand, maximum elongation of TiB2/Al composites was about 100%, but the flow stresses of TiB2/2017, TiB2/1N90 and TiB2/Al-Mg composites are the same value as those of TiN/2017, TiN/1N90 and TiN/Al-Mg, respectively although the flow stress of TiB2/2014 is larger than those of TiN/2014. It is thought that HSRS of TiN/2014 aluminum composite is effected by small amount of alloy elements to build optimum partial melting phases at the interfaces and grain boundaries.

Fundamentals of Advanced Materials For Energy Conversion: Hydrogen & Tritium Storage II - Complex Hydrides

Sponsored by: Extraction & Processing Division, Process Fundamentals Committee

Program Organizers: Renato G. Bautista, University of Nevada-Reno, Department of Chemical and Metal Engineering, Reno, NV 89557-0136 USA; Dhanesh Chandra, University of Nevada-Reno, Metallurgical & Materials Engineering, Reno, NV 89557 USA

Wednesday PM	Room: 613
February 20, 2002	Location: Washington State Conv. & Trade Center

Session Chairs: Karl Gross, Sandia National Laboratories, Analytl. Matls. Sci. Dept., PO Box 969, MS9403, Livermore, CA 94551-0969 USA; Renato G. Bautista, University of Nevada-Reno, Metlgcl. & Matls. Eng., Mackay Sch. of Mines, MS 388, Reno, NV 89557 USA

2:00 PM Invited

Complex Hydrides for Light-Weight Hydrogen Storage: *Karl J. Gross*[1]; E. H. Majzoub[1]; G. Sandrock[1]; [1]Sandia National Laboratories, Analytl. Matls. Sci., PO Box 969, MS9403, Livermore, CA 94551-0969 USA

An on-board supply of high-purity hydrogen is requisite for the development of fuel cell powered vehicles. The discovery that hydrogen can be reversibly absorbed and desorbed from catalyst-enhanced complex hydrides (the alanates) has created an entirely new prospect for lightweight hydrogen storage[1]. Unlike the common interstitial metal hydrides, these compounds release hydrogen through a series of decomposition reactions. The breakthrough for storage applications is that chemical doping with Ti, Zr and other transition metals allows these reactions to take place reversibly under moderate conditions. First investigations have focused on NaAlH4 which has a theoretical reversible hydrogen capacity of 5.5 wt.%. Phase transitions and crystal structure modifications were observed using X-ray powder diffraction during in situ thermal decomposition of this compound. Doping procedures have been dramatically improved through a dry mechanical milling process using TiCl3 as a precursor. Direct synthesis combined with dry doping has completely eliminated hydrocarbon contaminants found in previous wet doping techniques. This is critical for PEM fuel cell applications. Reversible capacities of nearly 5 wt.% at 125°C are now being achieved at rates required for many hydrogen storage applications. [1] Bogdanovic and Schwickardi, J. Alloys and Compounds Vol. 253,1 (1997).

2:30 PM Invited

Mechanochemically Induced Solid-State Transformations of Complex Aluminohydrides: *Vitalij K. Pecharsky*[1]; Viktor P. Balema[2]; [1]Ames Laboratory, Dept. of Matls. Sci. & Eng., Iowa State University, Ames, IA 50011-3020 USA; [2]Ames Laboratory, Iowa State University, Ames, IA 50011-3020 USA

Recent interest in complex aluminohydrides as potential near ambient, ultra-high capacity, solid-state sources of hydrogen (e.g., for fuel cells) calls for an improved understanding of the processes occurring in these hydrogen-containing materials during both the release and the uptake of hydrogen. Lithium aluminohydride ($LiAlH_4$) rapidly releases 5.2 wt.% of hydrogen (i.e., nearly four times more than $LaNi_5$-based alloys) during mechanochemical processing at ambient conditions in the presence of transition metal catalysts. Using a variety of solid-state characterization techniques, the mechanochemical transformations in a series of $LiAlH_4$-metal catalyst systems have been examined and preliminary insights on their mechanism have been obtained. Surprisingly, the well-known hydriding-dehydriding catalysts, such as Ni and Pt, are practically inactive in the mechanochemical dehydriding of $LiAlH_4$. The latest developments within this extended family of materials will be discussed.

3:00 PM

Hydrogen Absorbing Properties and Crystal Structure of Ti-V-Mn BCC Solid Solution Alloys: *Yumiko Nakamura*[1]; Etsuo Akiba[1]; [1]National Institute of Advanced Industrial Science and Technology (AIST), Energy Elect. Inst., AIST Tsukuba Central-5, 1-1-1, Higashi, Tsukuba, Ibaraki 305-8565 Japan

Ti-V based ternary BCC solid solution alloys are eminently suitable for use in on-board hydrogen storage. We have been focusing particularly on Ti-V-Mn BCC solid solutions since they show a phase transition distinguished from other BCC alloys: they form a mono-hydride and a di-hydride subsequently. Thus we investigated the crystal structure of the two kinds of hydrides by X-ray and neutron powder diffraction. As a result, it was found that both hydrides have an FCC metal sublattice. However, hydrogen atoms occupy the O-sites in the mono-hydride (NaCl structure), in contrast, they occupy the T-sites in the di-hydride (CaF2 structure). The Ti-V-Mn alloys forming NaCl type mono-hydrides show two plateaus in the P-C isotherms. This makes the hydrogen-solution region narrow and increases the effective hydrogen storage capacity.

3:30 PM Break

3:45 PM Invited

Solid State ^{1}H, ^{27}Al, and ^{23}Na NMR Studies of Doped and Undoped $NaAlH_4$: Kristin K. Kumashiro[1]; Walter Niemczura[1]; *Craig M. Jensen*[1]; [1]University of Hawaii, Dept. of Chem., Honolulu, HI 96822 USA

The dehydriding of solid $NaAlH_4$ is markedly accelerated and rendered reversible at moderate conditions upon mixing the hydride with a few mole percent of selected transition metal complexes. Since the initial report of this effect by Bogdanovic in 1997, the hydrogen cycling performance of the doped hydride has been the subject of intensive investigation and practical improvements. It now appears that doped $NaAlH_4$ could possibly be developed as a viable means for the onboard storage of hydrogen. However, the nature of the dopants has remained an enigma. Also a fundamental understanding of why the kinetic enhancement results upon doping is lacking. In order to elucidate the changes that occur upon doping, we have conducted solid-state NMR studies employing range of single- and double-resonance techniques. We have observed unexpected spectral features that will be discussed in the context of structural models.

4:15 PM Invited

High-Pressure Hydrides of Iron and its Alloys: *V. E. Antonov*[1]; M. Baier[2]; V. K. Fedotov[1]; B. Dorner[3]; G. Grosse[2]; A. I. Kolesnikov[1]; E. G. Ponyatovsky[1]; G. Schneider[2]; F. E. Wagner[2]; [1]Institute of Solid State Physics RAS, 142432 Chernogolovka, Moscow Dist. Russia; [2]Technische Universitaet Muenchen, Physik-Dept. E 15, D-85747 Garching Germany; [3]Institut Laue-Langevin, BP 156, 38042 Grenoble, Cedex 9 France

Hydrides of iron and iron-based alloys are thermodynamically stable only at high hydrogen pressures exceeding a few GPa and rapidly loose hydrogen under ambient conditions. Nevertheless, these hydrides can be retained in a metastable state at atmospheric pressure and low temperatures, if previously cooled at the high pressure to liquid nitrogen temperature. The review will discuss the current state of studies on phase transformations in the Fe-H and related systems and also on the composition, crystal structure and physical properties of the hydrides, both under high hydrogen pressures and in the "quenched" metastable state at ambient pressure. The studies at ambient pressure include magnetization measurements, X-ray and neutron diffraction, Mössbauer and neutron spectroscopy.

4:45 PM Invited

The Measurement and Analysis of the Kinetics of Hydride Formation in Bulk Metallic Samples: *Joseph Bloch*[1]; [1]Nuclear Research Center-Negev, Phys., PO Box 9001, Beer Sheva 84190 Israel

The hydriding of bulk metals and alloys is a gas-solid reaction in which a hydride product layer is initially nucleated adjacent to the gas-solid interface and continues to grow until a complete transformation of the parent (alpha) phase into the hydride phase. The combination of measurements of the overall hydriding kinetics of samples having defined shapes and dimensions, together with examinations of partially hydrided samples, enables the presentation of the reaction rate in terms of an appropriate reaction model. A common and important type of topochemical development of the hydride in bulk metals and alloys involves a hydride layer formed on the metallic surface. The continuity of the layer can affect the reaction rate. The rate of hydrogen absorption in a sample, in the presence of a hydride layer, is usually analyzed using a model combining several sequential steps in which the hydrogen is transferred from the gas phase into the reaction site. Coupling the flux equations across the layer under proper steady state conditions, results in a complex rate equation in which the steady state rate of hydrogen absorption (proportional to the hydride layer velocity) is expressed in terms of the pressure, temperature, the rate constants of the sequential steps and the critical concentrations of hydrogen in the hydride. Generally, the rate constants of the individual microscopic processes are comparable in magnitude, so that the overall rate is not controlled by any of the specific sequential steps. However, there are two limit cases related to the first stage, the adsorption, for which the general rate equation is much simpler, namely, the fast and the slow adsorption approximations. Using this limit cases, equations are derived for the steady state hydriding rate of a given system. These equations provide means to anticipate the pressure dependence of the steady state absorption rate under low pressures, close to Peq and under very high pressures. At the low pressure regime both the fast and slow absorption cases yield linear pressure dependence. For the very high pressure range, it is found that the rate become independent of the applied pressure. The rate is given then by a combination of the individual rate constants of the system and the critical hydrogen concentrations. The model is shown to apply in several real cases, such as ZrCo, LaNi5 and titanium.

5:15 PM
Catalytic Mechanism of Reversible Hydrogen Storage by Titanium-Doped Lithium Alanates: *Jun Chen*[1]; H. T. Takeshita[1]; H. Tanaka[1]; T. Kiyobayashi[1]; N. Takeichi[1]; T. Sakai[1]; [1]National Institute of Advanced Industrial Science and Technology, Special Div. of Green Life Tech., Ikeda, Osaka 563-8577 Japan

The alkali metal alanates such as MAlH4 and M3AlH6 (M = Li, Na) have high hydrogen capacity and low material cost, but their hydride formations and decompositions are irreversible, thereby making them impractical for industrial application. The recent work showed that doping alkali metal aluminum hydrides with titanium, zirconium, or iron could form reversible hydrogen storage systems. Surprisingly, effective mechanistic explanation for the catalytic phenomenon is not available. Thus, the aim of this article is to prepare Ti-doped MAlH4 and M3AlH6 (M = Li, Na) with nanocrystallites by means of ball milling and chemical synthesis, and to study their effects on dehydriding and rehydriding properties. The methods of X-ray diffraction (XRD), scanning electron microscopy (SEM), thermogravimetry (TG), and differential scanning calorimetry (DSC), and X-ray photoelectron spectroscopy (XPS) were used. It is found that the reversible hydrogen storage characteristics, depending on how to prepare them, are related to the catalytic activity of the doped Ti state. The result shows that both the homogenous distribution of Ti-catalyzed nanocrystallites and the Ti-catalyst with an electron attacking of Ti0 Û Ti4+ (Ti0/Ti3+/Ti4+) defect site take the role to be optimizing the reversible hydrogen storage.

Fundamentals of Structural Intermetallics: Fatigue and Fracture of TiAl

Sponsored by: ASM International: Materials Science Critical Technology Sector, Structural Materials Division, Jt. Mechanical Behavior of Materials
Program Organizers: Young-Won Kim, UES, Inc., Materials & Processing Division, Dayton, OH 45432 USA; Kwai S. Chan, Southwest Research Institute, Department of Materials Science, San Antonio, TX 78284 USA; Vijay K. Vasudevan, University of Cincinnati, Department of Materials Science and Engineering, Cincinnati, OH 45221-0012 USA

Wednesday PM — Room: 615-616
February 20, 2002 — Location: Washington State Conv. & Trade Center

Session Chairs: Kwai S. Chan, Southwest Research Institute, Dept. of Matls. Sci., 6220 Culebra Rd., San Antonio, TX 78284 USA; Chong-Soo Lee, Pohang University of Science and Technology, Matls. Sci. & Eng., San 31, Hyoja-dong, Pohang 790-784 Korea

2:00 PM Invited
An Experimental Study of Fatigue Crack Initiation in Lamellar Gamma Titanium Aluminides: *Andrew H. Rosenberger*[1]; [1]Air Force Research Laboratory, Matls. & Mfg. Direct., AFRL/MLLMN, 2230 Tenth St., WPAFB, OH 45433-7817 USA

The damage tolerant design philosophy encouraged by the US Air Force, as documented Engine Structural Integrity Program, requires that aeroengine components be lifed based an understanding of the fatigue and fatigue crack growth behavior of the material. The structural application of advanced intermetallic materials will require an application of this philosophy. However, the stress-life fatigue curve for gamma titanium aluminides is very flat while the fatigue crack growth rate versus stress intensity factor curve is very steep. These indicate that crack initiation plays a dominant role in the their fatigue failure. Hence, an understanding of the mechanism of crack initiation is paramount in their structural application and the development of new, advanced alloys. This study examined the mechanisms of crack initiation in lamellar gamma TiAl under fatigue loading and found significant differences compared to the cracking phenomena observed in monotonic tension or compression.

2:30 PM
Effects of Surface Crack and Notch Condition on the Fatigue Life of Lamellar TiAl Alloys: *Ze-Wen Huang*[1]; Stephen John Trail[2]; Paul Bowen[1]; [1]The University of Birmingham, IRC in Matls./Sch. of Metall. & Matls., Elms Rd., Edgbaston, Birmingham B15 2TT UK; [2]Cosworth Racing, Ltd., The Octagon, St. James Mill Rd., Northampton NN5 5RA UK

Both coarse-grained and fine-grained lamellar TiAl alloys have been studied to determine the high cycle fatigue (HCF) performance for a number of surface and notch conditions. All alloys studied have provided good HCF resistance in plain-sided and polished condition. The ratio of ãFL/ã0.2 is around 0.7-0.8 for fine-grained alloys and even >1 for a coarse-grained alloy. However, the surface damage caused by electro-discharge machining and the sensitivity to notches are found to be strongly dependent on lamellar colony size. The fine-grained alloys were much more sensitive to surface cracks and notches than the coarse-grained alloy, while notch sensitivity reduces as a result of notch strengthening at the notch root due to localised micro-plastic deformation. The difference in surface and notch sensitivity is explained based on a change in controlling mechanism for crack initiation and propagation, owing to a change in lamellar colony size and therefore a change in yield strength.

2:50 PM
Cyclic Stress-Strain Behaviour of a Cast Gamma-Titanium-Aluminide Alloy: *Anne-Lise Gloanec*[1]; Gilbert Hénaff[1]; Denis Bertheau[1]; Mustapha Jouiad[1]; [1]ENSMA, LMPM, 1, ave. Clement Ader, Teleport 2-BP 40109, Futuroscope, Chasseneuil 86961 France

Gamma titanium aluminide alloys have attractive high temperature properties which make them excellent candidates for aeronautical applications. The present study was undertaken in order to investigate the low cycle fatigue behaviour of the cast alloy Ti-48Al-2Cr-2Nb (atomic %) with a lamellar structure. Tests were carried out at a constant strain rate of 10-3s-1, at two temperatures (room temperature and 750°C) with different total-strain-amplitudes (from 0.2% to 0.8%), in air. The strain ratio (Re=emin/emax) values of -1 and 0 were used. The cyclic-stress-strain behaviour is characterised by an important hardening at room temperature and no hardening and no softening at 750°C. At both temperature a Bauschinger effect was noticed. In order to correlate the cyclic-stress-strain behaviour with fundamental deformation mechanisms, TEM observations have been undertaken. In particular the respective role of twining and dislocations cells is examined with respect to temperature and mechanical loading parameters.

3:10 PM
R-Curves for Toughness and Fatigue Crack Propagation in Gamma-TiAl: The Effect of Microstructure: *Reinhard Pippan*[1]; Andreas Tesch[1]; Manuel Beschliesser[2]; H. Kestler[3]; [1]Austrian Academy of Sciences, Erich Schmid Inst. of Matls. Sci., Jahnstrasse 12 A-8700 Austria; [2]University of Leoben, Inst. für Metallkunde und Werkstoffprüfung, Franz-Josef-Strasse 18, Leoben Austria; [3]Plansee AG, Reutte Austria

The increase of both-fracture and fatigue resistance as a function of crack extension-is studied in different Gamma-TiAl microstructures. Ti-46.5 at% Al-4at% (Cr, Nb, Ta, B) sheets-a fine grained near microstructure and coarse grained designed fully lamellar microstructures with different lamellar spacing are investigated. The basic idea of the applied technique is to start the toughness or fatigue crack growth experiments on pre-cracked specimens with a minimum contribution of crack tip shielding (or of extrinsic contributions to the fracture resistance). In order to minimize the effects of pre-cracking, we used specimens with very sharp notches (root radius about 10µm) and very short pre-cracks (lengths between 10-50µm) produced at the smallest possible cyclic compression loading. The influence of the microstructure on the intrinsic toughness and intrinsic fatigue mechanism as well as the increase of extrinsic mechanisms are presented and discussed.

3:30 PM
High Cycle Fatigue Properties of a Pre-Alloyed PM TiAl Alloy: Thomas Virginie[1]; Popoff Fabienne[1]; *Thomas Marc*[1]; [1]ONERA, DMMP, 29 ave. de la Division Leclerc, BP72, Chatillon, Cedex 92322 France

Based on our collaborative studies aimed to develop a competitive processing route for near-net shape TiAl components using Powder Metallurgy (PM), there is still a need to establish whether interstitial contamination may be harmful in specific cyclic conditions of aerospace gas turbine engines. Pre-alloyed powders of composition Ti-47Al-2Cr-2Nb have been produced by inert gas atomization. Higher interstitial contamination has been detected both in the smallest and largest powder particles. HCF tests were conducted at RT in air on a series of powder compacts consolidated by HIP. Low data scatter in the as-HIPed condition reflects no clear incidence of powder size on fatigue properties. Results also indicated that this PM material exhibits a particularly high endurance limit by comparing to other gamma materials tested under similar conditions. Detailed SEM fractography was carried out to identify the fracture initiation mechanisms. The possibility for an initial withdrawal of the most contaminated powder particles before consolidation was finally addressed in the present paper.

3:50 PM Invited

Thermo-Mechanical Fatigue Properties of Ti-46.5Al-5Nb: Hongfu Xiang[1]; Yuyou Cui[1]; *Rui Yang*[1]; Jinlong Wen[2]; Shouxin Li[2]; Rui Xu[3]; [1]Institute of Metal Research, CAS, Titanium Alloy Lab., 72 Wenhua Rd., Shenyang 110016 China; [2]Institute of Metal Research, CAS, State Key Lab. for Fatigue & Fracture of Matls., 72 Wenhua Rd., Shenyang 110016 China; [3]Liaoning Technical University, Dept. of Matls. Sci. & Eng., Fuxin 123000 China

Fatigue properties are of primary concern for gamma titanium aluminide alloys intended for off-ground component applications. For many low-risk, stationary applications the alloy is subject to the joint action of cyclic thermal and applied stresses. In this work the thermomechanical fatigue behavior of cast Ti-46.5Al-5Nb with fully lamellar microstructure was studied using smooth bar samples, under synchronized temperature and load control. Triangular and trapezoidal wave forms were used for 200~600°C and 300~700°C cycling in air, respectively, with the maximum load varying in the range of 0.71~0.97 of the ultimate tensile strength of the alloy. Slightly better fatigue life was found under the trapezoidal test condition than the triangular. This was interpreted as a result of creep deformation blunting the fatigue crack tip. Crack initiation and growth were characterized by examining tested samples and will be discussed in relation to microstructure and cast defects.

4:20 PM

Microscopic Characterisation of Gamma-TiAl Diffusion Bonded Joint Interfaces: *Cesar Justino Buque*[1]; Uwe Lorenz[1]; Stefan Eggert[1]; Fritz Appel[1]; [1]GKSS Research Centre Geesthacht, Institute for Materials Research, D-21502 Geesthacht Germany

The present paper is addressed to the problems which occur at the bond interfaces of diffusion bonded titanium aluminide alloys. The investigations were performed on Ti-45Al-10Nb (TNB alloy), Ti-45Al and Ti-54Al by SEM combined with EBSP analysis and EDX analysis. During the diffusion bonding static and dynamic recrystallisation occurs, which is controlled by the chemical composition and microstructure of the starting material. For instance, bonds of the TNB alloy have fine alpha-2 grains which are surrounded by gamma grains. The gamma grains exhibit preferentially middle orientations in the direction perpendicular to the bond interface. The induced alpha-2 particles are formed by the dissolution of alpha-2 lamellae during the recrystallisation process. The investigations showed, that high titanium content is necessary for alpha-2 grains to form during the bonding process. The recrystallisation process is associated with incompatibilities of elastic deformation. The resulting local stresses are relaxed by mechanical twinning and dislocation glide.

4:40 PM

Atomistic Simulations of Fracture in Lamellar Titanium Aluminides: Ashwin A. Ramasubramaniam[1]; *William A. Curtin*[1]; Diana Farkas[2]; [1]Brown University, Div. of Eng., Providence, RI 02912 USA; [2]Virginia Tech, Dept. Matls. Sci., Blacksburg, VA 24060 USA

Atomistic studies of fracture in lamellar Ti-Al are reported. Cracks in Ti3Al lamellae blunt; few dislocations reach the TiAl. Cracks in TiAl emit dislocations that arrest at the Ti3Al interface and then cleave. Cracks at the TiAl/Ti3Al interface blunt and deflect into the TiAl. A model for blunt crack dislocation emission and cleavage, extended to include blunting and shielding by dislocations, predicts (i) the number of dislocations at cleavage scales linearly with lamellar thickness t and (ii) the toughness scales with the square root of t. The simulations on TiAl agree with these scalings; results for Ti3Al can also be rationalized. Thin layers of TiAl between Ti3Al lamellae are thus the "weak links" controlling fracture in fully lamellar Ti-Al. Use of these nanoscale results in microscale models of fully lamellar Ti-Al to predict macroscopic crack growth and toughness are discussed.

5:00 PM

The Effect of Single and Multiple Overloads on the Fatigue Crack Growth of High Strength Titanium Aluminides: *Timothy Paul Halford*[1]; Paul Bowen[1]; [1]The University of Birmingham, Dept. of Metall. & Matls., Edgbaston, Birmingham B15 2TT UK

Samples of fully lamellar titanium aluminides with randomly orientated colonies were exposed to single and multiple overloads. The damage caused by these exposures was monitored by acoustic emission to determine its extent, its microstructural location, and the manner in which it is introduced in single and cyclic loading. The samples were then exposed to cyclic fatigue loading to failure, revealing the effect of overload damage upon fatigue life. The results were compared for alloys covering both fine and coarse-grained microstructures to identify mechanisms of initiation and growth.

5:20 PM

Production of Gamma-TiAl Sheets with Improved Superplastic Properties by Pack Rolling: *Marat R. Shagiev*[1]; Gennady A. Salishchev[1]; F. H. (Sam) Froes[2]; [1]Institute for Metals Superplasticity Problems of Russian Academy of Sciences, 39 Khalturin Str., Ufa 450001 Russia; [2]University of Idaho, Inst. for Matls. & Adv. Proc., Mines Bldg., Rm. 321, Moscow, ID 83844-3026 USA

The sheets of γ-TiAl based alloys with improved superplastic properties are of a great interest for aerospace applications. Such properties can be achieved through the grain refinement to micron and submicron level. Grain refinement may also lead to considerable decrease in the temperature intervals of brittle-to-ductile transition and, consequently, of pack rolling. Therefore, the smaller the grain size in rolling preform and the lower the rolling temperature, the higher superplastic properties in the sheet. Besides the microstructure improvement in γ sheets, decrease in rolling temperature will decrease their cost because of energy savings and use of the cheap can materials. The temperature intervals of pack rolling of several γ alloys were defined based on tensile properties at strain rates corresponding to rolling ones. Optimization of texture and rolling regimes were performed in order to eliminate anisotropy of superplastic properties in the sheet. Pack rolling temperature of Ti-50Al alloy with homogeneous microcrystalline structure was found to be 950°C while that of Ti-45Al-2Cr-2Nb-0.45B alloy was 1100°C. At 1000°C and strain rate of 10^{-3} s^{-1}, both sheets exhibited elongations of about 200% and steady state flow stresses of 140 MPa.

Fundamentals of Structural Intermetallics: Structural Intermetallics

Poster Session: Wednesday 6:00 PM – 9:00 PM

The Thermal Phase Stabilization Process of Wurtzite Boron Nitride: *Ali Solaiman Alwatban*[1]; [1]Riyadh Technical College, Mechl. Tech., PO Box 53699, Riyadh 11593 Saudi Arabia

Boron and nitrogen are the two elements that form boron nitride compounds of which a number of polymorphs exist. Hexagonal boron nitride (hBN) has the same structure as graphite, with boron and nitrogen atoms arranged alternately. The chemical bonds between boron and nitrogen within the layer are strong and covalent (sp2). On the other hand, the chemical bonds between the atoms in adjacent layers are weak (van der Waals type). One of the most common form of boron nitride which can be derived from the hexagonal form is wurtzite. In this paper the x-ray diffractometry, transmission electron microscopy and ESR spectroscopy have been utilized in order to investigate the phase stabilization process of wurtzite boron nitride, and the effect of the phase transformation of wurtzite boron nitride into a cubic form (cBN) under high.

Microstructural Evolution of PST-Titanium Aluminum during Microstrain Compression at 1023 K: *Abhishek Gupta*[1]; *Jörg M.K. Wiezorek*[1]; [1]University of Pittsburgh, Matls. Sci. & Eng., 848 Benedum Hall, Pittsburgh, PA 15261 USA

The creep resistance of lamellar TiAl appears to be related to the "soft" mode behavior, which is considered to be unaffected by the presence of the lamellar interfaces, yet lamellar refinement improves the creep strength. The present systematic study investigates the microstructural evolution and interface related deformation processes active during elevated temperature loading of lamellar TiAl. The evolution of microstructures in PST TiAl during constant low strain rate loading along "soft" and "hard" orientations at 750°C was studied by scanning and transmission electron microscopy. Deformation modes active under these different loading conditions and changes in morphology and microstructural metrics of the lamellar phases have been determined. Instability mechanisms operative at such straining and temperature conditions have been identified. Implications for the deformation behavior of PST-TiAl are discussed. Financial support from the School of Engineering of the University of Pittsburgh is acknowledged.

Carburisation and Metal Dusting of Fe-Al Alloys: *André Schneider*[1]; [1]Max-Planck-Institut für Eisenforschung GmbH, Matls. Tech., Max-Planck-Str. 1, Duesseldorf 40237 Germany

Iron aluminides are known for their resistance to high temperature oxidation and sulphidation. Only little information is available about carburisation and metal dusting of Fe-Al alloys. Carburisation ($a_C < 1$) and metal dusting ($a_C > 1$) experiments with Fe-Al samples were conducted in CO-H_2-H_2O and CH_4-H_2 gas mixtures at 800°C. The kinetics of the carbon transfer was measured using thermogravimetric analysis. Computer simulations using the software DICTRA have been conducted in order to predict the formation of the carbides M_3C, MC, M_3C_2 and k-carbide (Fe_3AlC_x) during carburisation. In these calculations the carbides were treated as dispersed particles in the Fe-Al-X (X = Ti, V, Nb) matrix.

Anomalous Effects of Alloying with Nb on Yield Strength of MoSi2: *Adel A. Sharif*[1]; Amit Misra[1]; Terence E. Mitchell[1]; [1]University of Michigan-Flint, Eng., 303 E. Kearsley St., MSB, Rm. 213, Flint, MI 48502 USA

The effects of alloying with 1 at% Nb on the yield strength of MoSi2 were investigated from room temperature to 1600°C. Anomalous solid solution softening at low temperatures and rapid solid solution hardening at high temperatures were observed by alloying. The mechanisms resulting in these anomalies were investigated. Ambient temperature softening may be attributed to the effects of Nb on stabilizing the 1/2<111> dislocations with lowering the stacking fault energy. At elevated-temperatures, dislocation substructures were consistent with a viscous-glide controlled behavior in (Mo,Nb)Si2 alloys as compared to the easy cell structure formation in unalloyed MoSi2. At the intermediate (600-1200°C) temperature range, the anomalous increase in the yield strength observed in unalloyed MoSi2 appears to be suppressed by Nb alloying.

Phase Transformations in the Synthesis of Intermetallics and Composites: *B. A. Greenberg*[1]; *E. P. Romanov*[1]; *L. A. Rodionova*[1]; *E. V. Shorohov*[2]; [1]Institute of Metal Physics Ural Division RAS, 18 S. Kovalevskaya, GSP-170, Ekaterinburg 620219 Russia; [2]Russian Federal Nuclear Center-VNIITF, Snezhinsk 456770 Russia

The microstructure of alloys produced by explosion loading of powders of pure metals and nanocrystalline diamond was examined. A quasispherical loading scheme with a conservation capsule was used. The stress on the contact surface was 50 GPa. Alloys Ni3-Al, Ti3-Al and TiAl were synthesized. Some characteristic microstructures were revealed, which could serve as indicators of the processes taking place in the conservation chamber under explosion loading. The chains of transformations were reconstructed for each synthesized alloy. The system under study was captured in a kind of a trap and failed to reach the equilibrium state. The presence of nanocrystalline diamond had a considerable effect on phase transformations during explosion loading. Fragments of the corresponding phase diagrams, which included both intermetallic reactions and formation of carbides, were reconstructed. Diamond was graphitized. The graphitization process was accompanied by appearance of carbon nanostructures, such as onion-like carbon structures, etc. The outlooks for a wider use of the alloys as functional materials thanks to the introduction of carbon nanostructures have been discussed.

Phase Transformations in Hydrogenated Ti-Nb: *Daniela Zander*[1]; David Olson[1]; Dan Eliezer[2]; [1]Colorado School of Mines, Dept. of Metlgcl. & Matls. Eng., Golden, CO 80401-1887 USA; [2]Ben-Gurion University of the Negev, Dept. of Matls. Eng., POB 653, Beer-Sheva 84105 Israel

The fabrication of Ti-based alloys can be strongly enhanced with hydrogen as a temporary alloying element; for example due to lower stresses and/or lower temperatures. Further in refractory metals or alloys hydrogen has a large potential to promote superplasticity. Until now very few results are known about the non-equilibrium conditions of phase transformations in Ti-Nb alloys due to hydrogen charging at high fugacities as well as from the gas phase. The objective point of our present research is to investigate in detail the influence of hydrogen on the phase stability in Ti-Nb (20-45 wt.% Nb) alloys. The influence of hydrogen on Ti-Nb was studied by means of TDA and microhardness test; the microstructure was investigated by x-ray diffraction, SEM and TEM. Hydrogenation of Ti-Nb was found to exhibit a significant effect on the microhardness. Hydrogen influences strongly the slip mechanism in the bcc-phase and assists in lowering the deformation energy. So the hydrogen influence on the mechanism of plastic deformation of Ti-Nb is of considerable interest. The observed microstructural investigations are expected to provide significant conclusions on the microstructural mechanism how hydrogen influences the plasticity of Ti-Nb. Furthermore the influence of deformation on the hydrogen absorption and desorption behavior as well as microstructural transformations of Ti-Nb are studied and discussed in detail.

The Protection and Creep Behavior of Ti Aluminides with (TiAlCr) Coatings: *German Fox-Rabinovich*[1]; George Weatherly[1]; David Wilkinson[1]; Anatoliy Kovalev[2]; Christoph Leyens[3]; Da Xu[1]; [1]McMaster University, Matl. Sci. & Eng., 1280 Main St. W., Hamilton L8S 4L7 Ontario; [2]Surface Phenomena Research Group, Metallophysical Institute, CNIICHERMET, 9/23 2-nd Baumanovskaya St., Moscow 107005 Russia; [3]DLR-German Aerospace Center, Inst. of Matls. Rsrch., Cologne D-51170 Germany

Ternary TiAlCr alloys have recently attracted attention as protective coatings for the gamma Ti-aluminide family of alloys due to their excellent oxidation stability in air at elevated temperatures. The common feature of these alloys is the formation of a stable alumina layer at the surface during oxidation. Two ternary compounds have been studied extensively, i.e. Ti0.25Al0.67Cr0.08 (t-phase) and Ti0.28Al0.44Cr0.28 (Laves-phase) and their behavior compared to the alumina forming binary Ti0.25Al0.75 (b-phase) alloy. We have shown that in order to achieve an oxidation resistance greater than the binary TiAl3 the components in a multi-component alloy must interact synergistically during oxidation. Cr alloying increases the activity of Al in the alloy and, equally important, reduces the Ti activity, thus establishing the thermodynamic driving force for Al2O3 to form. Cr therefore forces other elements to act together and form a protective alumina layer on the surface. Preliminary results will also be presented showing how coatings made from these alloys behave during flexural creep testing.

Reactive Processing of Nickel-Aluminide Intermetallic Compounds: *Hexiang Zhu*[1]; Reza Abbaschian[1]; [1]University of Florida, Dept. of Matls. Sci. & Eng., PO Box 116400, Gainesville, FL 32611 USA

NiAl have been fabricated by reactive sintering compacts of ball-milled powder mixtures containing Ni and Al. The reaction mechanism, as well as phase and microstructural development, was investigated by quenching the compacts from different temperatures during reactive hot compaction, and analyzed by XRD, SEM and EDS. It was found that the reaction process was strongly affected by pressure, heating rates, heat loss from the sample to the environment. The application of 50MPa prior to the reaction resulted in the intermetallic-formation reaction initiating at a temperature (480°C) much lower than that (~550°C) when no pressure was applied. At high heating rate (50°C/min), when the heat loss is small, the formation of NiAl occurs rapidly via combustion reaction. On the other hand, if the heat loss is significant, as in slow heating rate (10°C/min), the reaction process is slow and controlled by solid-state diffusion. The phase formation sequence for the slow solid-state reaction was determined to be: NiAl3, Ni2Al3, NiAl, NiAl (Al-rich) + Ni3Al, NiAl.

Quantitative Analysis on Boundary Sliding and its Accommodation during Superplastic Deformation of Two-Phase Ti3Al-xNb Intermetallics: *Ji Sik Kim*[1]; Young Won Chang[2]; Chong Soo Lee[2]; [1]Sangju National University, Dept. of Adv. Matls. Eng., Gajang-dong 386, Sangju, Kyung-buk 742-711 S. Korea; [2]POSTECH, Dept. of Matl. Sci. & Eng, San 31, Hyoja-dong, Pohang, Kyung-buk 790-784 S. Korea

A study has been made to investigate boundary sliding and its accommodation with respect to the variation of grain size and a/b volume fraction during deformation of two-phase Ti3Al-xNb intermetallics. Step strain rate tests and load relaxation tests have been performed at 950, 970 and 990°C to obtain the flow stress curves and to analyze the deformation characteristics by the theory of inelastic deformation. The results show that, due to the dislocational accommodation of both a and b phase, the accommodation modes for fine and coarse-grained materials are in good agreement with the mixed mode of the isostress and isostrain-rate models. The sliding resistance analyzed for the different boundaries is lowest in the a/a boundary, and increases on the order of a/a << a/b = b/b, which plays an important role in controlling the superplasticity of the alloys with various a/b phase ratios.

Phase Stability of L12-Based Alloys in Al-Ti-Cr System: *J. K. Lee*[1]; M. W. Oh[1]; M. H. Oh[2]; D. M. Wee[3]; [1]KAIST, Dept. of Matls. Sci. & Eng., Taejon 305-701 Korea; [2]Kumoh National University of Technology, Dept. of Matls. & Eng., 188, Sinpyung-dong, Kumi, Kyungbuk 730-701 Korea; [3]The Center for Advanced Aerospace Materials, POSTECH, Dept. of Matls. Sci. & Eng., Knut, Kumi 730-701 Korea

Compressive tests on Al-21Ti-23Cr (L12+Cr2Al), Al-21Ti-15Cr (L12+Al17Cr9) and Al-30Ti-15Cr (L12+TiAl+TiAlCr) alloys were performed to investigate the effects of alloy composition on the phase stability of L12-based alloys below 1000°C. In Al-30Ti-15Cr alloy with relatively higher Ti content, yield strength increased very significantly after exposure at 800°C than other two alloys. Microstructure observation and phase identification confirmed that Al-30Ti-15Cr alloy with Ti-rich composition exhibited the full decomposition of L12 phase after exposure at 800°C despite the partial decomposition of L12 phase in Al-21Ti-23Cr and Al-21Ti-15Cr alloys with Ti-lean composition under same conditions. This results from the fact that L12 phase field was shifted to the direction of Al-rich corner composition with decreasing temperature in Al-Ti-Cr phase diagram. In three-point bend tests to investigate the correlation between phase stability and fracture toughness, the fracture toughness of Al-30Ti-15Cr alloy was more degraded after exposure at 800°C than other two alloys because Al-30Ti-15Cr alloy exhibited poor phase stability due to higher Ti content. This elucidated that the poor phase stability resulted in the degradation of fracture toughness of L12-based alloys. Therefore, L12-based alloys with lower Ti content would be more appropriate by considering phase stability coupled with fracture toughness.

Composites of Iron Aluminides Containing Al_2O_3 and TiC: *Joachim H. Schneibel*[1]; S. C. Deevi[2]; [1]Oak Ridge National Laboratory, Metals & Cer. Div., PO Box 2008, Oak Ridge, TN 37831-6115 USA; [2]Chrysalis Technologies, Inc., Richmond, VA USA

Sintered and injection molded parts based on iron and stainless steel powders are extensively used around the world for a variety of industrial applications such as tool bits, fasteners, gears, and various automotive components. Composites based on iron aluminides offer high hardness, excellent wear resistance, and good oxidation and corrosion resistance. In this paper we discuss the processing techniques, microstructure, and mechanical properties of FeAl-based composites such as FeAl/Al_2O_3 liquid phase-sintered with and without transition metal carbides. While FeAl does not wet Al_2O_3, addition of TiC to FeAl/Al_2O_3 improves the wetting. Because of residual porosity, the room temperature flexure strength of a FeAl-16.5TiC-16.5Al_2O_3 (vol. %) composite produced by liquid phase sintering was only 300 MPa. Further processing by hot forging at 1000°C removed the residual porosity and increased the strength to 1000 MPa. Interestingly, the Al_2O_3 and TiC particulates did not degrade the fracture toughness significantly and room temperature values of 27 MPa $m^{1/2}$ were observed. Research at the Oak Ridge National Laboratory (ORNL) was sponsored by Chrysalis Technologies Incorporated under the Work for Others Program, IAN 14B480501, US Department of Energy under contract DE-AC05-00OR22725 with UT-Battelle, LLC.

Intermetallic Compounds in Diffusion Couples of Fe with an Al-Si Eutectic Alloy: *Shant Prakash Gupta*[1]; [1]Indian Institute of Technology, Matls. & Metlgcl. Eng., I. I. T. Kanpur, Kanpur, UP 208 016 India

The phase equilibria in the Fe-Al-Si system have been studied in the temperature range 1020 to 1115°C using ternary diffusion couple experiment involving pure Fe and high purity Al-Si eutectic alloy. A number of binary and ternary Intermetallic compounds have been observed in the diffusion couples cooled at different rates from the annealing temperatures. The microstructure and composition of the Intermetallic compounds have been described and compared with the results published earlier. In all, nine ternary Intermetallic compounds have been identified. Except for the tau3 and tau5 phases, compositions of tau1, $\tau2$, tau4, tau6, tau7, tau9, tau10 phases agree quite well with the work of Murav'eva and coworkers. The tau8-phase composition has not been observed in this investigation which may be due to very high Si in the intermetallic compound. The invariant reactions originally proposed by Takeda et al are postulated to be responsible for the observed microstructures. The tau10 phase has been observed only in diffusion couples rapidly cooled from the annealing temperature and is proposed to be a metastable phase.

Control of Phase Transformation Process and Improvement of Shape Memory Effect in NiAl Martensite Including Ternary Elements: *S. H. Kim*[1]; M. H. Oh[2]; D. M. Wee[3]; [1]KAIST, Dept. of Matls. Sci. & Eng., Taejon 305-701 Korea; [2]Kumoh National University of Technology, Dept. of Matls. & Eng., 188, Sinpyung-dong, Kumi, Kyungbuk 730-701 Korea; [3]The Center for Advanced Aerospace Materials, POSTECH, Dept. of Matls. Sci. & Eng., Knut, Kumi 730-701 Korea

The Ni-rich b-NiAl alloys, which are potential materials for high temperature shape memory alloys, show the thermoelastic martensite transformation, and it can make their shape memory effect. But the transformation to Ni5Al3 phase occurring at 450~550°C during heating of NiAl martensite interrupts the reversible martensite transformation, consequently the shape memory effect in NiAl martensite can't show any more. The phase transformation process in binary Ni-(33~37)Al martensite was investigated by DTA, and we could understand that the condition of reversible martensite transformation was not the b-Ni5Al3 transformation but the M-Ni5Al3 transformation occurring at 250~300°C. Therefore the transformation temperature of M-Ni5Al3 determined the critical temperature of shape memory effect. For verifying the critical temperature, the phase transformation process was investigated for various ternary Ni-33Al-X alloys (X = Cu, Co, Fe, Mn, Cr, Ti, Si, Nb). As a result, Ti, Si and Nb addition was very effective to lower the Ms temperature, and they could help the Ni-33Al-X alloys to have the shape memory effect. Especially Si and Nb addition could raise the transformation temperature of M-Ni5Al3, and it would be helpful for the shape memory effect at higher temperature.

Mechanical Properties of Fully Lamellar TiAl-Mo-V-Si Alloy: *Sadao Nishikiori*[1]; [1]Ishikawajima-Harima Heavy Industries Company, Matl. Tech. Dept. Rsrch. Inst., 3-1-15 Toyosu, Koutou-ku, Tokyo 135-8732 Japan

In general, refractory metals regard as the beta stabilizer. Increasing of these elements leads to produce a fully-lamellar structure with the beta phase surrounding lamellar colonies. This microstructure has not been attributed to the increase in creep strength. Influence of alloying on microstructure and creep behavior in the TiAl-Mo-V-Si alloy was investigated. Then, as-cast and heat treated microstructures were analyzed as well crept samples. As a result, we developed the fully-lamellar alloy which shows a creep rupture life of well over 2160ks at 1073K and 220MPa and the minimum creep rate of 2x10-5 h-1 at 1073K and 200MPa. Moreover, effect of the micro-alloying of carbon on the lamellar colony size and creep resistance in this developed alloy was also discussed. In addition, with an industrial view to applications, this work mentions castabilty on sub-production scale and effect of surface reaction formed during casting on fatigue properties.

Processing of Ruthenium Aluminide Alloys: *Sebastien Rosset*[1]; David R. Johnson[1]; [1]Purdue University, 1289 Materials & Electrical Engineering Bldg., W. Lafayette, IN 47907-1289 USA

Ruthenium aluminide (RuAl) is a promising high temperature structural material due to its high temperature melting point and room temperature toughness from qualitative tests. However, this unusual room temperature toughness remains unexplained due to lack of single crystal deformation work. Promising results have been found on preliminary experimentations using arc-zone melting. Large grains of several millimeters in diameter have been obtained when growing samples of 50.5 and 52 at% Al. Furthermore, microstructure analysis suggests that a ruthenium-ruthenium aluminide liquid film forms at the grain boundaries and promotes a fast grain growth. Additionally, an advantage of this technique is that it does not require melting of the whole sample. Present work is focused on the control of parameters such as composition and microstructure in order to obtain single crystal specimens suitable for compression and bending tests.

Characterization of the Microstructure and Properties of Welded TiAl Sheet Materials: *Shenavia Wilkerson*[1]; Mario Arenas[1]; Viola L. Acoff[1]; [1]The University of Alabama, Metlgcl. & Matls. Eng., Box 870202, Tuscaloosa, AL 35487-0202 USA

Two gamma TiAl sheet materials were investigated to characterize the weld microstructure and mechanical properties. Spot welding was performed on the design fully lamellar materials. Each specimen cracked catastrophically immediately after welding. Preliminary results showed that all cracks were parallel to the direction of rolling. There were also some smaller cracks within the fusion zone. The primary annealed material was used for making butt welds. For the specimens welded transverse to the rolling direction, there were cracks parallel to the welding direction (normal to the rolling direction) and the cracking was much more severe than those for the specimens welded in the longitudinal direction. The fusion zone hardness of the transverse specimens was slightly lower than that for the longitudinal samples. This corresponded to a coarser fusion zone microstructure for the transverse samples. For the specimens investigated, a preliminary weld structure-property relationship will be established as a function of texture.

Tensile Properties of HVOF-Sprayed Iron Aluminide Coatings: *Terry C. Totemeier*[1]; Richard N. Wright[1]; W. David Swank[1]; [1]INEEL, PO Box 1625, MS 2218, Idaho Falls, ID 83415 USA

The tensile properties of Fe3Al coatings produced by High-Velocity Oxy-Fuel (HVOF) thermal spraying have been investigated at room and elevated temperature using 0.75 mm-thick dogbone specimens. Coatings were sprayed onto steel substrates at three particle velocities. Residual stresses in the coatings were characterized by curvature measurements and X-ray diffraction; subgrain sizes and microstrains were measured using X-ray line broadening analysis. Tensile tests were performed at room temperature on coatings in the as-sprayed condition and after annealing at 800C for two hours. As-sprayed coatings were also tested at 700C. The fracture stresses of the coatings at room temperature increased with increasing particle velocity and were markedly higher after the annealing treatment. The coatings showed no ductility at room temperature. The coating strengths were considerably reduced at high temperature, and plastic deformation occurred. The variations in tensile properties with particle velocity and annealing treatment correlate with changes in microstructure and residual stress state.

The Nitridation of Iron Alumindes in a H2/NH3/Ar Gas Mixture: *Wu Kai*[1]; H. Y. Tsai[1]; H. H. Hsieh[1]; J. P. Chu[1]; [1]National Taiwan Ocean University, Inst. of Matls. Eng., 2, Pei-Ning Rd., Keelung 20224 Taiwan

The nitridation behavior of pure Fe and two iron aluminides (Fe-28 and -40 at.%Al) was studied over the temperature range 500-700°C in a H2/NH3/Ar gas mixture. The results indicated that the nitridation kinetics of both pure Fe and iron aluminides followed the parabolic rate law. The nitridation rates of iron aluminides decreased with increasing Al content and temperature. The scales formed on pure Fe consisted of mostly Fe4N and minor Fe3N, while the scales formed on Fe-Al alloys were a heterophasic mixture of mostly Fe4N and minor amounts of Fe3N and AlN. The formation of AlN is responsible for the reduction of the nitridation rates of pure iron. This work was supported by the National Science Council of Republic of China under the Grant No. NSC 89-2216-E-019-008.

Ordered Beta and Omega Phases in Highly Alloyed, High Strength TiAl Alloys: *Ze-Wen Huang*[1]; Wayne Voice[2]; Paul Bowen[1]; [1]The University of Birmingham, IRC in Matls./Sch. of Metall. & Matls., Elms Rd., Edgbaston, Birmingham B15 2TT UK; [2]Rolls-Royce plc, Aeros Grp., PO Box 31, Derby DE24 8BJ UK

TiAl alloys with significant additions of refractory metals, such as Nb, Zr and W, have been developed aimed at increasing the liquidus temperature thus improving high temperature strength and creep resistance. It has been found that ordered beta and omega phases form in as-cast highly-alloyed TiAl alloys which have a detrimental effect on mechanical properties. The retained beta and omega phases can be removed by HIPping in some alloy systems but both phases reform when subjected to long-term exposure at 700°C. On the other hand, alloys containing ordered beta and omega show no further reduction in mechanical properties after long-term thermal exposure. In order to understand the specific behaviour of ordered beta and omega, a detailed study has been conducted for highly alloyed, high strength TiAl alloys. The effects of retention, removal, re-formation, and Oswald coarsening of ordered beta and omega on mechanical properties are discussed.

General Topics in Waste Treatment and Minimization: Resource Reclamation and Contaminant Control

Sponsored by: Extraction & Processing Division, Process Mineralogy Committee, Waste Treatment & Minimization Committee
Program Organizers: Junji Shibata, Kansai University, Department of Chemical Engineering, Osaka 564-8680 Japan; Cheryl Dahlin, US Department of Energy, Albany Research Center, Albany, OR 97321-2152 USA; Jasper Kwong, US Department of Energy, Albany Research Center, Albany, OR 97321-2198 USA

Wednesday PM	Room: 604
February 20, 2002	Location: Washington State Conv. & Trade Center

Session Chairs: Cheryl L. Dahlin, US Department of Energy, Albany Rsrch. Ctr., 1450 Queen Ave. S.W., Albany, OR 97374 USA; Jasper Kwong, US Department of Energy, Albany Rsrch. Ctr., 1450 Queen Ave. S.W., Albany, OR 97374 USA

2:00 PM
Common Elements of Industries that Successfully Recycle/Reuse Spent Refractory Material: *James P. Bennett*[1]; Kyei-Sing Kwong[1]; [1]Albany Research Center-USDOE, 1450 Queen Ave. S.W., Albany, OR 97306 USA

The successful reuse/recycling of refractory materials after removal from industrial service is limited because of contamination, the low value of spent materials, the low cost of virgin raw materials, the lack of driving forces such as regulations or taxes, and low disposal costs. Most spent refractory is disposed in landfills. Concerns over future liability for waste materials, corporate images, and ISO 14000 have helped to encourage recycling at some companies. The recycling practices and applications for spent refractory materials at facilities successfully recycling used refractory materials will be discussed, with emphasis on similarities among them.

2:20 PM
Reclamation of Spent Lost-Wax Casting Molds: *Cheryl L. Dahlin*[1]; David C. Dahlin[1]; [1]US Department of Energy, Albany Rsrch. Ctr., 1450 Queen Ave. S.W., Albany, OR 97321 USA

The practicality of reclaiming lost-wax or investment-casting mold materials for reuse or recycling depends upon numerous technological, economic, energy, quality, social, and regulatory considerations, which can involve different issues than are faced by conventional sand-casting operations. Experimental reclamation tests employing mineral-processing techniques to beneficiate spent mold materials into reusable and/or recyclable components were done on materials from three lost-wax casting operations. Bench scale beneficiation tests using conventional minerals-processing technology were unsuccessful in producing reusable investment mold components at acceptable grade and recovery. Intimate association of phases makes liberation difficult and requires expensive leaching to produce reusable slurry materials. However, this investigation suggests that mineral beneficiation can separate spent mold components into potentially marketable concentrates. Concentrates of facecoat materials, structural iron, casting metal splash, and ceramic refractory were successfully produced by the experimental processes. A preliminary conceptual process flowsheet was developed based on the findings of the investigation.

2:40 PM
Treatment of Electronic Scrap: *Derek J. Fray*[1]; Robert W. Gibson[1]; [1]University of Cambridge, Dept. of Matls. Sci. & Metall., Pembroke St., Cambridge CB2 3QZ UK

The quantity of electronic scrap will continue to expand in the foreseeable future and there may be a need to be able to recycle used printed circuit boards, together with the components. At the present time, the two most common methods of processing electronic scrap are landfilling of feeding the material into furnaces and recovering the majority of the metals. In both these methods, the actual value of the components is lost. This paper reports a method for the selective dissolution of the solder that allows the components to be recovered which can then be sorted by value, usefulness or toxicity. The leachant can then be electrolysed to recover the solder, the boards shredded and copper and precious metals recovered. Experimental results will be presented confirming the validity of this approach.

3:00 PM Discussion

3:20 PM Break

3:40 PM
Spent Pot Lining (SPL)Treatment and Fluoride Recycling Process: *Ken Mansfield*[1]; [1]Portland Aluminium, Spent Pot Lining, PB 1, Portland, Victoria 3305 Australia

Spent Pot Lining (SPL) is a hazardous waste product from the smelting of aluminium due to it's fluoride and cyanide content. Disposal of SPL is a major problem for the aluminium industry due to disposal by landfill increasingly being banned. Between 1992-94 Portland Aluminium, Alcoa and Ausmelt conducted trials in Ausmelt's demonstration furnace to treat SPL. From these trials, and work with CSIRO to produce aluminium fluoride from the furnace offgases, Portland Aluminium and Alcoa authorised AUD$24,000,000 in 1995 to construct an SPL treatment facility. Output products from the process are aluminium fluoride, which has been successfully trialed in the aluminium smelting process instead of imported material, and a vitreous granulated slag having leachability qualities acceptable to the EPA for specific end uses. The "SPL Treatment and Fluoride Recycling Process" at Portland, Australia is successfully treating SPL and converting it into useful products.

4:00 PM Cancelled
Oxidative Ageing of Chromium(III) Bearing Land Disposed Slags and Possible Prevention: Kriveshini Pillay

4:20 PM
Selective Flocculation of Western Phosphate Tailings: *Cathy A. Summers*[1]; David C. Dahlin[1]; Keith Prisbrey[2]; [1]US Department of Energy, Albany Research Ctr., 1450 Queen Ave. S.W., Albany, OR 97321 USA; [2]University of Idaho, Dept. of Metlgcl. & Mining Eng., Moscow, ID 83844-3024 USA

Western phosphate cyclosizer overflow tailings were processed by selective flocculation to recover an upgraded phosphate product. Feed slurries contained 5 to 9 pct solids by weight and had P_2O_5 grades between 14 and 16 pct; in bench-scale tests, they were treated with dispersant and flocculant(s) at slightly elevated pH to selectively flocculate the silicate minerals. Under the best conditions, dispersed products contained 25 to 26 pct P_2O_5 and recovered from 19 to 37 pct of the total P_2O_5. The pilot-scale demonstration used on-line analysis of P_2O_5 grade to close the feedback control loop for reagent additions and confirmed bench-scale results.

High Performance Metallic Materials for Cost Sensitive Applications: Metal Matrix Composites

Sponsored by: Structural Materials Division, Structural Materials Committee, Titanium Committee

Program Organizers: Edward Y. Chen, TiTech International, Inc., Pomona, CA 91768 USA; Rod Boyer, Boeing Commercial Airplane Group, Seattle, WA 98124-2207 USA; F. H. (Sam) Froes, University of Idaho, Institute of Materials and Advanced Processes, Moscow, ID 83844-3026 USA; Eric M. Taleff, University of Texas, Mechanical Engineering Department, Austin, TX 78712-1063 USA

Wednesday PM	Room: 213
February 20, 2002	Location: Washington State Conv. & Trade Center

Session Chair: Lu Li, National University of Singapore 119260 Singapore

2:00 PM
Novel Al-RE High Temperature Materials for Aerospace Applications: *Shihong Gary Song*[1]; [1]United Technologies Research Center, Matls. & Proc., 411 Silver Ln., E. Hartford, CT 06108 USA

Most conventional aluminum alloys suffer from long-term exposure to elevated temperatures and therefore are rarely used above 175°C due to a sharp decrease in strength with increasing temperature. In practice, titanium and nickel based superalloys are routinely utilized for structural applications in the temperature regime of 175 ~350°C. They are, however, considered overkill in many cases and inevitably lead to high costs and weight penalties. Aluminum alloys or composites can be used in place of titanium and superalloys, provided that the strength of the former is enhanced in the temperature regime. To this end a strengthening mechanism other than precipitation has to be employed, which should be temperature insensitive. In this light, new and cost-effective aluminum materials utilizing dispersion strengthening are being developed at the United Technologies Research Center, which have demonstrated promising properties for elevated temperature applications.

2:20 PM
In-Situ Synthesis of Al/TiC Master Alloy Grain Refiners by Different Methods: *B. Q. Zhang*[1]; L. Lu[1]; M. O. Lai[1]; H. S. Fang[1]; [1]National University of Singapore, Dept. of Mechl. Eng., 10 Kent Ridge Crescent, 119260 Singapore

Al/TiC master alloy is a potential grain refiner for aluminium and aluminium alloys. However, the difficulty in the synthesis of TiC particles and thus the relatively higher production cost of Al/TiC have led to a great obstacle for its practical application in the aluminium industry. A new method has been developed for the in-situ synthesis of TiC and the preparation of Al/TiC master alloys. In the present paper, Al/TiC master alloys were prepared by the conventional method and the newly developed method respectively. By using chemical analysis, X-ray diffraction phase analysis (XRD) and scanning electronic microscope (SEM), it was found that, in the conventional method, TiC particles synthesized at two temperatures of 850ºC and 1250°C accompanied by serious oxidation of aluminum melt, which introduces large number of oxide inclusions in the master alloys. While in the new method, the synthesis process was much accelerated and plenty of TiC were synthesized in a shorter period at a low temperature of 850ºC. The synthesis mechanism was discussed in details in this paper.

2:40 PM Cancelled
Fabrication and Characterization of Aluminum–Fly Ash Composites: *Ruby Zhang*

2:40 PM
Microstructures and Mechanical Properties of Pure Al Matrix Composites Reinforced with Al-Cu-Fe Quasicrystal Particles: *Fei Tang*[1]; Iver E. Anderson[1]; Bulent Biner[1]; [1]Ames Laboratory, Ames, IA 50011 USA

Model composite materials were produced by using a powder metallurgy technique from either commercial purity or high purity Al matrix powders, reinforced with 30 vol.% Al-Cu-Fe quasicrystal particles, where all powders had dia. < 10µm. The tensile and yield strength of this model composite material was improved 111% and 220%, respectively, compared to the pure Al matrix values for each matrix powder. Elastic modulus (ultrasonic measurements) of the both composites is very close to the theoretical upper bound value from the rule of mixtures. The modulus and microstructure results on fractured specimens are consistent with good interface bonding between the quasicrystals and both Al matrix types. Use of high purity Al matrix powder from a gas atomization reaction synthesis (GARS) technique resulted in improved sintering, as shown by Auger interdiffusion layer measurements, and enhanced tensile ductility. A load transfer mechanism appears to be the main strengthening mechanism for these Al/QXL composites because the CTE of Al and Al-Cu-Fe quasicrystal are relatively low. Project funding from DOE-BES under contract number W-7405-Eng-82.

3:00 PM
Synthesis of TixAly-Al2O3-TiC Composites from TiO2, Al and C Powders: *Z. H. Cai*[1]; Deliang Zhang[1]; [1]University of Waikato, Dept. of Matls. & Proc. Eng., PB 3105, Hamilton New Zealand

Bulk TixAly-Al2O3-TiC composite materials have been successfully synthesized by using a combination of high energy mechanical milling, chemical reactions among TiO2 and C and Al and sintering. It has been demonstrated that this process is very effective in producing composites with Al3Ti, TiAl and Ti3Al matrices and different volume fractions of Al2O3 and TiC reinforcement particles. The reinforce particle size and morphology of the reinforcement particles are significantly influenced by the sintering conditions, especially the sintering temperature. It has been found that during sintering the coarsening of TiC particles is significantly slower than that of Al2O3 particles, resulting in a small TiC particle size in the final microstructure of the composites. The small TiC particle size is highly favorable in improving the strength and fracture toughness of the composites. This paper will present and discuss the results of this study which includes phase formations as a result of different chemical reactions, microstructural development of the materials during sintering, and the effect of microstructure on the strength and fracture toughness of the composite materials.

3:20 PM Break

3:40 PM

Amorphous and Nanostructured Ti-Based Alloys: *Adrian Jianu*[1]; Eberhard Burkel[1]; [1]Rostock University, Phys. Dept., Aug.-Bebel-Str. 55, Rostock D-18051 Germany

The formation and stability of amorphous and nanocrystalline phases in multicomponent Ti-based alloys and composites were studied using high-resolution X-ray diffraction experiments, electron microscopy, differential scanning calorimetry and in situ temperature/pressure synchrotron radiation diffraction experiments. The substitution of titanium with silver significantly enhances the formation of amorphous or nanostructured phases during rapid solidification. Addition of small amounts of Ce in Ti53Zr27Ni20 alloy composition leads to an enhancement of the nucleation rate of the icosahedral phase. When amounts of Ce are added, the icosahedral phase becomes disordered tending to amorphisation and to the formation of a nanocrystalline CeNi intermetallic compound. The addition of Sc in Ti-based alloys generated a mixture of two nanograin phases with C14, respectively quasicrystalline icosahedral structure. Alternative lower-cost processes have been investigated like non-equilibrium synthesis (rapid solidification, mechanical alloying and field assisted sintering) in order to establish the technology and know-how for new Ti-based material system processing.

4:00 PM

Reaction Synthesis of Ti/TiC Particulate Reinforced Composite by Powder Metallurgy Processing: *Hyungsik Chung*[1]; Yong-Hyun Kim[1]; Yong-Jin Kim[2]; [1]Ajou University, Molecular Sci. & Eng. Dept., San 5, Wonchun-dong, Paldal-gu, Suwon, Kyonggi Province 442-749 Korea; [2]Korea Institute of Machinery and Materials, Matls. Eng., 66 Sangnam-dong, Changwon, Gyungnam Province 641-010 Korea

TiC particulates were synthesized in a porous titanium compact by reacting a blended elemental Ti-alloy powder compact with a hydrocarbon gas such as methane or propane and sintering in a vacuum. Titanium carbide was formed as a thin layer around each particle surface during the reaction. Various transient carbides and hydride were also formed during the reaction but disappeared completely by a high temperature vacuum sintering, leaving only the titanium carbide globules. The volume percent of the carbides could be controlled precisely by adjusting the reaction temperature and time while the size and morphology of the carbides were mostly affected by the sintering temperature. Hipping or hot forging was employed to obtain fully densified composite after the sintering. The resulting structure shows uniformly distributed carbide particles, well adhered to the matrix. Tensile yield strength over 1000 MPa, elastic modulus over 130 GPa and 2% elongation were obtained with 10 vol.% TiC reinforcement at room temperature.

4:20 PM

Low Density Ti-Mg-B Alloys: *Mohsin Qureshi*[1]; Sunil Patankar[1]; F. H. (Sam) Froes[1]; [1]University of Idaho, Inst. for Matls. & Adv. Proc. (IMAP), Mines Bldg., Rm. 321, Moscow, ID 83844-3026 USA

Low density titanium alloys were synthesized by mechanical alloying with magnesium and boron. Boron was used because of its low density coupled with its ability to readily form boride with titanium. The microstructure evolution due to the milling process was investigated using optical microscopy, X-ray diffraction (XRD) and differential thermal analyzer (DTA). Ti-Mg-B powder mixture was found to undergo amorphization during mechanical alloying and was partially transformed into TiB2 during subsequent hot isostatic pressing. The resultant material was a composite material with the TiB2 phase dispersed in a Ti-Mg matrix.

4:40 PM

Synthesis of a Ti5Si3-Mo Alloy: *Fusheng Sun*[1]; F. H. (Sam) Froes[1]; [1]University of Idaho, Inst. for Matls. & Adv. Proc. (IMAP), Mines Bldg., Rm. 321, Moscow, ID 83844-3026 USA

A Ti5Si3-2Mo alloy was synthesized from blended elemental powders of Ti, Si and Mo by mechanical alloying. An incubation time exists for the formation of the Ti5Si3 alloys, and addition of Mo decreases the incubation time of theTi5Si3-2Mo alloy. XRD results show that the Mo was solid solutioned in the Ti5Si3 phase, and the c/a ratio of the Ti5Si3 phase decreases with the addition of Mo. After mechanical alloying for 8 hours, a nanometer alloy of Ti5Si3-2Mo was synthesized with a grain size of about 5nm. Phase transformations occurring in the system during mechanical alloying and heating were also studied with the use of DTA and XRD. During mechanical alloying, the grain size of alpha-Ti was refined, and the Si was solid solutioned in alpha-Ti. When an amount of stored energy (in the form of interfaces) was introduced by MA, the reaction of Ti5Si3 phase occurs by a form of self-propagating high-temperature synthesis (SHS).

WEDNESDAY PM

International Symposium on Science and Technology of Interfaces in Honor of Dr. Bhakta Rath: Semiconductors

Sponsored by: Structural Materials Division, ASM International: Materials Science Critical Technology Sector, Electronic, Magnetic & Photonic Materials Division, Physical Metallurgy Committee, Superconducting Materials Committee, Jt. Mechanical Behavior of Materials, Titanium Committee

Program Organizers: Sreeramamurthy Ankem, University of Maryland, Department of Material & Nuclear Engineering, College Park, MD 20742-2115 USA; I. Ovidko, Russian Academy of Sciences, Institute of Problems of Mechanical Engineering, Laboratory for Theory of Defects in Materials, St. Petersburg 199178 Russia; Chandra Pande, Naval Research Laboratory, Materials Science and Technology Division, Washington, DC 20375-5000 USA; S. Ranganathan, Indian Institute of Science, Department of Metallurgy, Bangalore 560 012 India

Wednesday PM	Room: 617
February 20, 2002	Location: Washington State Conv. & Trade Center

Session Chairs: Aris Christou, University of Maryland, Matls. Sci. & Eng., Bldg. 090, College Park, MD 20742-2115 USA; K. L. Murty, DMR, National Science Foundation, Metals Rsrch., 4201 Wilson Blvd., Arlington, VA 22230 USA

2:00 PM Invited

Gallium Nitride Epitaxy on (0001) Sapphire: *Subhash Mahajan*[1]; [1]Arizona State University, Cheml. & Matls. Eng., PO Box 876006, 1711 S. Rural Rd., Tempe, AZ 85287-6006 USA

Two-step epitaxy consisting of low temperature GaN nucleation layers (NLs) and high temperature (HT) GaN overgrowths, deposited on (0001) sapphire by metalorganic chemical vapor deposition, has been examined by transmission electron microscopy and atomic force microscopy. Results indicate that NLs consist of faceted crystalline islands that exhibit a spread in rotation about the (0001) axis. This structure undergoes a metamorphosis on annealing and evolves into rounded islands. The lateral growth during HT deposition of GaN occurs by the attachment of atomic species to steps associated with the rounded islands, resulting in faceted, flat top islands. It appears that growth occurs preferentially in certain regions which develop into "growth patches." These patches then grow vertically and laterally over the underlying substructure of NLs. The coalescence of these patches produces a continuous GaN layer. The origins of threading dislocations (TDs) in GaN layers has also been investigated. Results show that TDs do not form during the coalescence of islands as was assumed previously. Instead, three possible sources of TDs have been identified: (1) defects in NLs, (2) steps on island surfaces, and (3) point defects. Defects in the NLs constitute the major source and develop into TDs by glide and climb. Furthermore, TDs can form during the HT island growth stage because of sources (2) and (3). It has also been suggested that the mosaic structure observed in fully grown GaN layers is due to elastic interactions between TDs. As a result, TDs undergo glide and climb to form subgrain boundaries.

2:25 PM Invited

Epitaxial Issues and Growth Morphologies of InAlAs/InGaAs MQWs and Heterostructures on Non-(100) Index Substrates: *Aris Christou*[1]; [1]University of Maryland, Matls. Sci. & Eng., Bldg. 090, College Park, MD 20742-2115 USA

Substrate orientation: (100), (11)A, (110)B, (111)A, (111)B and (112) significantly affects phase decomposition and ordering. Through TEM, AFM and photoreflectance investigations, the effect of MBE growth on the above surfaces has been determined. Significant features related to phase decomposition due to (110)B, (111)B and (112) surfaces has been identified. Hexagonal defects in samples grown on (111) and (112) InP surfaces have been identified and correlated with optical measurements.

2:50 PM Invited

Nanoscale Phenomena of Synthetic Functional Oxide Heterostructures: Role of Interfaces: *R. Ramesh*[1]; [1]University of Maryland, Matls. Sci. & Eng., College Park, MD 20904 USA

Over the past six years, we have focused considerable effort on understanding the growth and characterization of functional oxide thin films and heterostructures, specifically ferroelectric, dielectric and magnetic perovskites. Using both epitaxial and polycrystalline materials on a variety of substrates as test vehicles, we have been carrying out systematic studies on the effect of composition, point defect chemistry, strain and processing variables on the microstructure and physical properties. A novel aspect of our work is the combined use of focused ion beam milling and scanning force microscopy techniques to understand the influence of film microstructure on the relevant properties at the nanoscale. This presentation will address two problems and approaches to understand and solve them: (i) the materials science of thin conducting barrier layers that enable the integration of the complex oxides on a silicon surface; (ii) domains in epitaxial films and mapping of their dynamics using scanned force microscopy. In this presentation, I will describe some possible areas where fundamental measurements in conjunction with theoretical studies and modeling will enable a better understanding of the complex phenomena involved in these materials, especially the role of structural, chemical and functional interfaces (such as domain walls). The work at Maryland is supported by the NSF-MRSEC.

3:15 PM Invited
The Role of Silicide Interfaces in Silicon Technology: *Francois Max d'Heurle*[1]; [1]IBM, Rsrch. Dept., PO 218, Yorktown Heights, NY 10598 USA

Silicon devices require metal contacts to make connections to the outside world. The silicides used for this application must satisfy a number of criteria relating to how their metallurgical and electrical properties modify the interface characteristics. The silicides used for this purpose usually result from metal-silicon reactions which can be significantly affected by the nature of the interface, epitaxial or not. Epitaxy with silicon stabilizes phases that do not exist under equilibrium conditions. In TiSi2, epitaxy with alloyed phases, enhances the formation of the desired C54 phase. Silicide grain boundaries constitute fast diffusion paths for metal or silicon atoms during the reactions themselves, and later on can be fast diffusion paths for dopant atoms. Extremely high density of stacking faults have been observed in some silicides with a structure and structural transformations akin to cobalt.

3:40 PM Invited
The Atomic-Scale Structure of Surfaces and Interfaces in III-V Semiconductor Devices: *Lloyd J. Whitman*[1]; [1]Naval Research Laboratory, Code 6177, Washington, DC 20375-5342 USA

NRL has a long-standing effort to develop novel optoelectronic and high-speed devices based on the "6.1 Å" family of semiconductors-InAs, GaSb, and AlSb. Many of these applications are based on heterostructures where the individual components are only several atomic layers thick, presenting a significant challenge to MBE growth technology. One way we are attacking this problem is by characterizing the surfaces and interfaces within the devices on the atomic scale using scanning tunneling microscopy. For example, we grow a number of samples differently, and then compare their material, optical, and electrical properties. Alternatively, we take a bottom-up approach, working to understand and optimize the surfaces and interfaces first and then apply this knowledge to a device. I will review our efforts to reach a fundamental understanding of all the competing physical and chemical processes during growth, and thereby develop knowledge-based strategies for optimizing the device fabrication.

4:05 PM Invited
Silicon-Germanium-Carbon Self Assembled Quantum Dot Growth and Applications in Electronic Memory Devices: *Sanjay Banerjee*[1]; [1]University of Texas, Austin, TX 78712 USA

We will discuss the growth of strain-engineered Si-Ge-C self-assembled quantum dots (SAQDs) via ultra-high vacuum chemical vapor deposition (UHVCVD) under varying conditions on various substrates including Si, SiO2 gate oxides, oxynitrides, and CVD high-K materials such as ZrO2, HfO2 and their silicates. There are interesting surface chemistry and physics issues in quantum dot growth under such circumstances involving the interplay between reactant precursor partial pressures, growth temperature, surface free energies, and strain energy in Si-Ge-C quantum dots. We will discuss a study of nucleation and grain growth by CVD in the binary/ternary alloys Si-Ge-C on the various types of gate dielectrics mentioned above. We will show how the compressive strain in Si-Ge can be compensated by the tensile strain using C, and how that impacts dot formation. The role of B and P doping will also be discussed. The use of a Scanning Tunneling Microscope to seed such quantum dot growth will also be described. We will also discuss our work on quantum dot flash memories using these Si and Ge nano-crystals as floating gates.

4:30 PM Invited
Diamond Surfaces and Interfaces: *James E. Butler*[1]; [1]Naval Research Laboratory, Chem. Div., Code 6174, Washington, DC 20375 USA

Synthetic diamond materials grown by chemical vapor deposition (CVD) impact a wide range of advanced technologies, ranging from industrial laser windows to high voltage electronics and power distribution. The chemistry of diamond surfaces is integral to the growth by CVD, surface electrical properties, and bonding to other materials. I will provide a summary of our current understanding of diamond surfaces and interfaces.

Lead-Free Solders and Materials Issues in Microelectronic Packaging: Fundamentals, Phases, Wetting and Surface Tension

Sponsored by: Electronic, Magnetic & Photonic Materials Division, Electronic Materials Committee, Electronic Packaging and Interconnection Materials Committee
Program Organizers: Srini Chada, Motorola, Department APTC, Fort Lauderdale, FL 33322 USA; Darrel R. Frear, Motorola, Tempe, AZ 85284 USA; Sung-Ho Jin, Lucent Technologies, Bell Laboratories, Murray Hill, NJ 07974 USA; Sung Kang, IBM, T. J. Watson Research Center, Yorktown Heights, NY 10598 USA; C. Robert Kao, National Central University, Department of Chemical Engineering, Chungli City, Taiwan; Michael J. Pfeifer, Motorola, Northbrook, IL 60062 USA; Martin Weiser, Honeywell Electronics Materials, Plated and Discrete Products, Spokane, WA 99216 USA

Wednesday PM	Room: 612
February 20, 2002	Location: Washington State Conv. & Trade Center

Session Chairs: Martin Weiser, Honeywell Electronics Materials, Spokane, WA 99216 USA; Michael Pfeifer, Motorola, 4000 Commercial Ave., North Brook, IL 60062 USA

2:00 PM Invited
A Study on Applying the Sn-3.9Ag-0.6Cu Solder to Electronic Packages with Ni Metallization: *C. E. Ho*[1]; C. Robert Kao[1]; [1]National Central University, Dept. of Cheml. & Matls. Eng., Chungli City 320 Taiwan

The 95.5Sn3.9Ag0.6Cu (wt.%, Sn3.9Ag0.6Cu) alloy is considered to be one of the most promising replacement for the Sn37Pb solder. The soldering pads in many electronic packages, such as BGA substrates or C4 devices, use Ni layer as a diffusion barrier. However, very few studies on the reaction between Sn3.9Ag0.6Cu solder and Ni substrate had been reported. The objective of this paper is to study the interactions between Sn3.9Ag0.6Cu solder and Ni during reflow soldering. In this study, the reaction kinetics of Sn3.9Ag0.6Cu/Ni at 225-275C was investigated. The effect of soldering temperature on the reactions was also studied in details.

2:25 PM
Surface Tension Measurements of the Eutectic Alloy (Ag-Sn 96.2 at.%) with Cu Additions: *Zbigniew Stanislaw Moser*[1]; Wladyslaw Gasior[1]; Janusz Pstrus[1]; Stanislaw Ksiezarek[2]; [1]Polish Academy of Sciences, Inst. of Metall. & Matls. Sci., Reymonta St. 25, Krakow 30-059 Poland; [2]Institute of Non-Ferrous Metals, Sowinskiego St. 25, Gliwice 44-101 Poland

Surface tension may be obtained from experiments or from modeling by Butler's method based on the optimized thermodynamic parameters. In our previous studies we have measured surface tensions for the entire range of concentrations and at the extensive temperature range for the binary liquid alloys: Ag-Sn,Ag-Bi,Bi-Sn,In-Sn and for the ternary additions of Zn, In and Bi to the binary eutectic (Ag-Sn 96.2 at.%). In this study we have measured surface tensions of (Ag-Sn 96.2 at.%) with following Cu additions: 0.5, 2, 3.75, and 6.5 at.% at the temperature range 227 to 927C. It was shown that the Cu additions increases surface tensions in the relation to the binary eutectic Ag-Sn. The same trend is observed by modeling of the surface tensions from optimized thermodynamic parameters reported in the literature. The 4th element alloying to near-eutectic Sn-Ag-Cu will be analyzed to decrease the surface tension and the melting temperature.

2:45 PM
Solder Balling of Lead-Free Solder Pastes: *Minna Arra*[1]; Dongkai Shangguan[2]; Eero Ristolainen[3]; Toivo Lepistö[4]; [1]Flextronics, Finlaysoninkuja 21 A, Tampere 33500 Finland; [2]Flextronics, 2090

Fortune Dr., San Jose, CA 95131 USA; [3]Tampere University of Technology, Elect., PO Box 692, Tampere 33101 Finland; [4]Tampere University of Technology, Matls. Sci., PO Box 589, Tampere 33101 Finland

Solder balling in reflow process for some of the Sn/Ag/Cu solder pastes was studied in this work. Three different solder pastes, several different reflow profiles and conditions and two stencil thicknesses were used in the investigation. During the process screening phase, the reflow profile was varied. Results show that flux chemistry and reflow atmosphere play the major role in solder balling. With all the pastes, the number of solder balls dropped close to zero when nitrogen atmosphere was introduced. Another finding was the influence of the stencil thickness on solder balling. With a thinner stencil, the number of solder balls increased significantly for two of the pastes. In the last phase, the effect of the solder paste particle size on solder balling was studied. One flux chemistry was chosen and the solder particle size was varied between type 3 and type 4. The results show that with type 4 ~40-140 % more solder balls are formed compared to type 3 paste.

3:05 PM
An Experimental Investigation of Solidification Response of Nanoparticle-Reinforced Tin-Lead Solder: *Guo-Xiang Wang*[1]; Dechao Lin[1]; Song Liu[1]; T. S. Srivatsan[1]; [1]The University of Akron, Dept. of Mechl. Eng., Akron, OH 44325-3903 USA

A series of experiments have demonstrated that nanopowders can be effectively used as a viable means for increase the strength of eutectic tin-lead solder, even for low percentages of the reinforcing nanopowders. This presentation will highlight experimental observations on solidification response of tin-lead solder blended with nanopowders. The solidification kinetics of the solder mixture, tin-lead powder mixed with either copper or titanium-dioxide nanopowders, was conducted on both copper substrate and aluminum substrate under controlled rates of cooling. It was generally observed that addition of nanopowders resulted in a refinement in the eutectic spacing of the solidified end product thus providing ample evidence for its influence in altering the kinetics of both nucleation and growth. The presentation will highlight a nucleation and growth theory that was used to rationalize microstructural development. Strength of the solidified end product was quantified through microhardness tests. Results reveal an increase in hardness of the composite solder, with addition of copper nanopowders having a significant influence than titanium-dioxide nanopowders.

3:25 PM Break

3:40 PM Invited
Phase Equilibria of the Cu-Ni-Sn System: Experiments and Modeling: *Gautam Ghosh*[1]; [1]Northwestern University, Dept. of Matls. Sci. & Eng., 2225 N. Campus Dr., Evanston, IL USA

The knowledge of the Cu-Ni-Sn phase equilibria is very important to understand the evolution interfacial microstructure of solder joints that employ Cu/Ni metallization schemes. In such cases the diffusion path or the interfacial microstructure can be strongly time dependent. To address these and other basic issues relevant to soldering, we have performed selected experiments to determine the phase equilibria of the Cu-Ni-Sn system that complement the existing results. To minimize the number of experiments, a comprehensive thermodynamic modeling of the ternary system is carried out. This allows the calculation of Cu-Ni-Sn phase diagrams at any temperature. Both experimental and calculated results in the temperature range relevant to soldering will be presented.

4:05 PM
Thermodynamics of the In-Sn-Zn System: *Jean-Pierre Bros*[1]; [1]Universite de Provence, CNRS UMR 6595, IUSTI, Technopoloe Chateau-Gombert, 5 rue Enrico Fermi, Marseille 13453 France

Lead+tin solder alloys are widely used in electronics industry because of their physical properties (low melting point, good corrosion resistance, correct electrical conductivity,. . .). But, because of the environmental issues related to lead, its use is restricted in many applications. Accordingly, much research is developing on new lead-free solders and tin-based multicomponent alloys including silver, zinc, indium, bismuth, antimony and/or copper appear to be the most promising substitutes. The melting point or the melting range of these new materials will be one of the most important requirements. The present paper reports such a thermodynamic approach: The enthalpy of formation and the phase diagram of the In-Sn-Zn ternary liquid system were measured over an extended composition range. This ternary enthalpy of formation was compared to that estimated from the [In-Zn], [Sn-Zn] and [In-Sn] binary liquid systems. The location of the liquidus surface and of the ternary eutectic plan have been precise. This new information, in good agreement with some results already published, allows the In-Sn-Zn phase diagram to be proposed.

4:25 PM
Experimental Determination and Thermodynamic Calculation of the Phase Equilibria and Surface Tension in the Sn-Ag-In System: *Xing Jun Liu*[1]; Yasuo Inohana[1]; Ikuo Ohnuma[1]; *Ryosuke Kainuma*[1]; Kiyohito Ishida[1]; *Zbigniew Moser*[2]; Wladyslaw Gasior[2]; Janusz Pstrus[2]; [1]Tohoku University, Dept. of Matls. Sci., Grad. Sch. of Eng., Sendai, Miyagi 980-8579 Japan; [2]Polish Academy of Science, Inst. of Metall. & Matls. Sci., Reymota St. 25, Krakow 30-059 Poland

The phase equilibria and liquidus surface in the Sn-Ag-In system are important for the design of the Pb-free solder, however, the phase equilibria in this system have not been well established. In the present paper the phase equilibria of the Sn-Ag-In system were investigated by means of differential scanning calorimetry (DSC) and metallography. The isothermal sections at 180-600C, as well as some vertical sections were determined. Thermodynamic assessment of the Cu-In-Sn system was also carried out based on experimental data of activity and phase equilibria using the CALPHAD method, in which the Gibbs energies of the liquid, fcc and bcc phases are described by the subregular solution model and that of compounds are represented by the sublattice model. The thermodynamic parameters for describing the phase equilibria were optimized, and agreement between the calculated and experimental results was obtained. The maximum bubble pressure method has been used to measure the surface tensions and densities of the In-Sn liquid alloys (25, 51.7 and 75 at. % In) at temperatures 227 to 927C. Similarly, there were investigated ternary alloys, adding 5 and 10 at.%In to the eutectic alloy (Ag-Sn 96.2 at.%) at the same temperature range as for the In-Sn alloys. Due to the similarity of both surface tension and density of pure In and Sn experimental data are scattered. In such cases, modeling of surface tension from optimized thermodynamic parameters by Butler's model is superior over experimental data, as shown in this contribution.

4:45 PM
Thermodynamic Investigations of Possible New Solder Alloys: *Adolf Mikula*[1]; [1]Institute of Inorganic Chemistry, Waehringerstrasse 42, Vienna A-1090 Austria

Lead-tin solders are commonly used in electronic packaging due to their unique combination of electrical, chemical, physical, thermal and mechanical properties. Since lead and lead containing alloys cause great environmental concern and health hazards it is necessary to replace lead in solder materials. To get the same or better properties it is therefore necessary to investigate some multicomponent systems. Some of these materials are ternary tin or indium alloys. Not much information about thermodynamic properties is known. We measured the thermodynamic properties of several ternary alloys like Au-Sn-Zn, Ag-Sn-Zn, Al-Sn-Zn, Cu-In-Zn and In-Sn-Zn. The free energy and the heat of formation were determined with an emf method and with calorimetric measurements over the whole composition range. These thermodynamic data were used to improve the phase diagram calculations and will be helpful for some theoretical models to improve the calculation of physical or mechanical properties.

5:05 PM
Strong Effect of Cu Concentration on the Reactions between SnCu Lead-Free Solders and Ni: W. Chen[1]; C. E. Ho[1]; *C. Robert Kao*[1]; [1]National Central University, Dept. of Cheml. & Matls. Eng., Chungli City 320 Taiwan

The eutectic Sn-0.7Cu solder is considered a very promising lead-free replacement for the Sn-37Pb solder, especially for wave soldering applications. For industrial uses, a ±0.2% accuracy in composition is generally accepted. In other words, for the Sn-0.7Cu solder, the Cu concentration can range from 0.5 to 0.9 weight percentage. However, our recent study revealed that the Cu concentration had a very strong effect on the reactions between Sn-Cu solders and Ni. One of the main reaction product $(Cu_xNi_{1-x})_6Sn_5$ showed a very rich morphology, depending on the exact Cu concentration. The morphology and distribution of $(Cu_xNi_{1-x})_6Sn_5$ would in turn have a strong influence on the strength of solder joints. This study showed that the Cu concentration must be controlled in a much tighter range than ±0.2% in applications involving Ni-bearing contacts and surface finishes.

Magnesium Technology 2002: Magnesium Alloy Processing and R&D Strategies

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

Program Organizers: Howard I. Kaplan, Magnesium Corporation of America, Salt Lake City, UT 84116 USA; Menachem Bamberger, Technion, Israel Institute of Technology, Haifa 32000 Israel; Byron B. Clow, International Magnesium Association, McLean, VA 22101 USA; Gerald S. Cole, Ford Motor Company, Ford Research Laboratories, Dearborn, MI 48121 USA; Rod Esdale; John N. Hryn, Argonne National Laboratory, Argonne, IL 60439-4815 USA; Zi-Kui Liu, Pennsylvania State University, Materials Science and Engineering, University Park, PA 16082-5005 USA; John L. Mihelich, Metal Experts International, Winston, GA 30187 USA; Ramaswami Neelameggham, Magnesium Corporation of America, Salt Lake City, UT 84116 USA; Eric A. Nyberg, Pacific Northwest National Laboratory, Materials Processing Group, Richland, WA 99352 USA; Mihriban O. Pekguleryuz, Noranda, Noranda Technology Centre, Pointe-Claire, Quebec H9R 1G5 Canada; Bob R. Powell, General Motor Corporation, NAO Research and Development Center, Warren, MI 48090-9055 USA; Allen Schultz, Hatch, Mississauga, Ontario L5K 2R7 Canada

Wednesday PM	Room: 606
February 20, 2002	Location: Washington State Conv. & Trade Center

Session Chairs: Menachem Bamberger, Technion, Israel Institute of Technology, Haifa 32000 Israel; Neale Neelameggham, Magnesium Corporation of America, 238 N. 2200 W., Salt Lake City, UT 84116 USA

2:00 PM Cancelled
Semi Solid Forming of Magnesium Alloys: An Innovative Route to Produce Advanced Components: Dierk C. Hartmann

2:20 PM
Evaluation of a New Concept for Semi-Solid Magnesium Billet Forming: *Basant L. Tiwari*[1]; Raja K. Mishra[1]; [1]General Motors, R&D Ctr., Matls. & Proc. Lab., MC 480-106-212, Warren, MI 48090-9055 USA

A new concept of using ternary eutectic for semi-solid magnesium billet forming was evaluated. Magnesium alloy ZC63 showed that the presence of only 16% liquid facilitated metal forming at low pressures and temperatures in the semi-solid state. It was also shown that the amount and composition of the liquid rich in the alloying elements did not change significantly with temperature. This feature will alleviate the problems caused by excessive oxidation of magnesium during reheating and handling of the billets. The new concept also provides a basis for designing new alloys exclusively suited for semi-solid billet forming.

2:40 PM
Tensile Coherency in Semi-Solid AZ91 Alloy: *John F. Grandfield*[1]; John Taylor[2]; Cameron Davidson[1]; [1]CRC for Alloy and Solidification Technology (CAST), CSIRO Mfg. Sci. & Tech., Albert & Raglan Sts., Preston, Victoria 3072 Australia; [2]The University of Queensland, Dept. of Mining, Minls. & Matls. Eng., St. Lucia, Queensland 4072 Australia

Hot tearing during casting is related to tensile loads applied to the semi-solid region. Recent attempts to horizontal direct chill cast magnesium alloy AZ91 resulted in typical centre-line hot tears. The tensile strength of AZ91 in the semi-solid region was therefore investigated. Results indicate that the tensile strength of the mush at high fraction solid is due to the strength of the bonded solid grains while at low fraction solid the tensile strength is related to the surface tension of the liquid film between the grains. Tensile coherency is estimated to occur at 85% fraction solid, at which point the solid grains become bonded.

3:00 PM
Advances in Thixomolding Magnesium: *Steve LeBeau*[1]; Jason Fulcher[2]; Oscar Roberto[3]; Robert Altham[4]; Randy Beals[5]; [1]Thixomat, Ann Arbor, MI USA; [2]DaimlerChrysler Corporation Auburn Hills-Michigan, MI USA; [3]Henkel Surface Technologies, Madison Heights, MI USA; [4]Keronite, Ltd. Advanced Surface Technology, Great Abington, Cambridge UK; [5]DaimlerChrysler Corporation, Cast Metals Eng. & Prototyping, 800 Chrysler Dr., Auburn Hills, MI 48326 USA

Thixomolding is a relatively new process in which the metallic slurry is injected into a die cavity at semi-solid temperatures to form near net-shape products from the solid feed stock. As part of on-going research regarding the Thixomolding process, this study concentrated on Thixomolded magnesium alloys AZ91D and AM60B. The test samples where made with high and low volume percent solid for each alloy. Each sample was benchmarked using an extensive test matrix that includes different material characteristics (tensile, hardness, microstructure, metallographic image analysis, x-ray, surface roughness, warp, linear thermal expansion, notched bar impact), joining (welding, riveting, adhesives) and finishing examinations (corrosion, pretreatment, e-coating, anodizing and Keronite, etc.) The database will be used to create a working model using the rule-of-mixture approach for the various properties. Future work will include examination of newly developed magnesium alloys for high temperature applications.

3:20 PM
Blended Magnesium Alloys Produced by the Thixomolding® Process: *T. K. Nandy*[1]; J. W. Jones[1]; T. M. Pollock[1]; D. M. Walukas[2]; R. F. Decker[2]; [1]University of Michigan, Ann Arbor, MI USA; [2]Thixomat, Inc., Ann Arbor, MI USA

Blended alloys consisting of mixtures of varying fractions of AM60B and AZ91D have been produced using the Thixomolding® technique. Alloys investigated included 100%AM60B, 67%AM60B + 33%AZ91D, 33%AM60B + 67%AZ91D and 100%AZ91D. The blended alloys were fabricated by first mechanically mixing chips of the two base alloys and Thixomolding® the blended mixtures. Molding parameters were adjusted in order to investigate the structure and properties of each of the four alloys under conditions of molding with low fractions of solid during the process (4-9%) as well as high fractions of solid (15-22%). At both low and high fractions of solid, the yield strengths and tensile elongations of the blended alloys were consistent with a Rule of Mixtures prediction. Microstructures have been examined in detail by optical and scanning electron microscopy. Additionally, energy and wavelength dispersive spectrometry have been utilized to examine chemical gradients in the mixed microstructures.

3:40 PM Break

4:00 PM
A Comparison of Aging Kinetics between a Die Cast and a Thixocast Magnesium Alloy: *Emanuela Cerri*[1]; Salvatore Barbagallo[1]; Marcello Cabibbo[2]; Enrico Evangelista[2]; [1]INFM-University of Lecce, Dept. Ingegneria dell'Innovazione, via per Arnesano, Lecce 73100 Italy; [2]INFM-University of Ancona, Dept. of Mech., via Brecce Bianche, Ancona 60131 Italy

The aging kinetics of two Mg-Al alloys were investigated by different techniques after various heat treatments. One alloy was produced by die-casting and the other by thixocasting. The material furnished in the as-thixocast state consists of large α-globules separated by quasi-eutectic phase ($\alpha+\beta$). The cast structure is formed by a dispersion of Mg-α grains and the eutectic ($\alpha+\beta$) where β is the $Mg_{17}Al_{12}$. Thermal analysis was performed on the two AZ91 alloys to define the temperature formation of the phases. Afterwards, the solution kinetics and the aging processes were followed by hardness, electrical conductivity and microscopy. The kinetics of aging are faster at the higher temperature due to the enhanced diffusion of atoms in the matrix, so the hardness peaks at 210-220°C occur after 3-4 h while at 170°C, the peaks are not reached in the time range considered. Differences arise in aging kinetics of the two magnesium alloys.

4:20 PM
Rapidly Solidified Powder Metallurgy Mg97Zn1Y2 Alloys with Tensile Yield Strength of 610 MPa and Elongation of 5%: *Yoshihito Kawamura*[1]; Akihisa Inoue[2]; [1]Kumamoto University, Dept. Mechl. Eng. & Matls. Sci., 2-39-1 Kurokami, Kumamoto 860-8555 Japan; [2]Tohoku University, Inst. for Matls. Rsrch., Sendai 980-8577 Japan

The RS powder metallurgy (P/M) magnesium alloys have been investigated for conventional alloys, resulting in no remarkable improvement in strength. Moreover, the RS P/M processing has been applied to amorphous alloys, in which the nanocrystalline P/M magnesium alloys were synthesized by the crystallization of the amorphous phase. The nanocrystalline RS P/M alloys exhibit excellent tensile strength, while the ductility is very poor for practical use. In order to develop high strength RS P/M magnesium alloys with enough ductility for practical use, it is necessary to investigate new alloy compositions suited to the RS processing. We have found that Mg-Zn-Y alloys were the most promising system for production of RS P/M alloys with high strength and good ductility, as consequence of the preliminary investigations of the alloy compositions in Mg-X1-X2 (X=Li, Al, Zn, Ca, Sn and Y) alloys using the melt-spun ribbons. Nanocrystalline magnesium alloys having high tensile strength, high elevated-temperature tensile strength, high-strain-rate superplasticity and high thermal stability have been developed in Mg97Zn1Y2 alloy by rapidly solidified powder metallurgy (RS P/M) processing. The tensile yield strength and elongation that were dependent on the consolidation temperature were in the ranges of 570 to 606 MPa and 5 to 15%, respectively. Young's modulus of the RS P/M alloy was 45 GPa. The specific tensile yield strength was four times as high as that of a commercial AZ91-T6 alloy, and was higher than those of conventional titanium (Ti-6Al-4V) and aluminum (7075-T6) alloys. The RS P/M alloys exhibited excellent elevated-temperature yield strength that was 500 MPa at 423 K. The RS P/M alloy also exhibited high-strain-rate superplasticity at a wide strain-rate range from 1x10-2 to 1x100 s-1 and at a low temperature of 623K. It is expected that the Mg97Zn1Y2 RS P/M alloy can be applied in some fields that requires simultaneously the high specific strength at ambient and elevated temperatures and high workability.

4:40 PM
Australian R&D on Magnesium Alloys: *Gordon Dunlop*[1]; [1]CAST, UDP No 055, Univ. of Queensland, St. Lucia, Queensland 4072 Australia

The current expansion of useage of magnesium alloys in automotive and electronics applications has led to a significant upsurge in the amount of R&D that is being undertaken on these alloys. Much of this R&D is addressing important challenges for the successful development of magnesium applications, such as: improved recycling technology; improved die casting technology; design expertise; property data bases; replacement of SF6 cover gas; improved high temperature alloys; coatings and corrosion resistance; joining technologies; wrought alloys and processes. CAST is an Australian cooperative research centre focussed on light metals. The centre involves research organisations, universities, manufacturers and light metals producers as its members. The presentation will focus upon work that is being undertaken in Australia and elsewhere in the world to develop a better understanding of magnesium alloys and improved technologies for their processing and application.

5:00 PM
Magnesium Die Casting Alloy Design: *Ketil Pettersen*[1]; Per Bakke[1]; Darryl Albright[2]; [1]Norsk Hydro ASA, Light Metals Rsrch. Ctr., PO Box 2560, N-3907, Porsgrunn Norway; [2]Magnesium Market Development, Hydro Light Metals, 39209 W. Six Mile Rd., Ste. 200, Livonia, MI 48152 USA

The properties of an alloy are closely linked to the compositional and processing parameters. Magnesium applications demand different critical properties, such as creep resistance for automotive drive train components, ductility and energy absorption in safety parts, and high yield strength in structural parts. Consequently, alloy design must be targeted to achieve specific microstructural features for the various application areas. In the alloy development process, thermodynamics is an important tool in identifying promising candidate compositions. However, the phase morphology and material grain size are not easily predicted. The experimental work of casting test samples and evaluating them in the laboratory is thus an inevitable part of building new knowledge about the relationships between composition, microstructure and properties. This paper presents some fundamental considerations for designing magnesium alloy compositions, as well as results from investigations of selected die cast alloy samples.

5:20 PM
Research Strategy for AM60B Magnesium Steering Wheel: *Shae K. Kim*[1]; Hyung-Jo Yoo[2]; Young-Jig Kim[1]; [1]Sungkyunkwan University, Sch. of Metall. & Matl. Eng., 300 Chunchun-dong, Jangan-gu, Suwon, Gyeonggi-do 440-746 Korea; [2]Donghwa Enterprize Company, Ltd.

Driven largely by the desire to reduce the weight of products, the automotive industry in Korea is predicting significant growth in the use of magnesium alloys. As one of these efforts to adopt magnesium alloys in car components, the paper describes the research strategy for high pressure die castings of AM60B magnesium steering wheel. Design and die casting process optimization for AM60B magnesium steering wheel will be explained compared to other magnesium steering wheels. Design/Structure/Property relationship will be also presented.

Materials Issues Related to the Collapse of the World Trade Center

Program Organizer: Toni Marechaux, National Research Council, National Materials Advisory Board, 2101 Constitution Ave. NW, Washington, DC 20418 USA

Wednesday PM	Room: 611
February 20, 2002	Location: Washington State Conv. & Trade Center

Session Chair: Toni Marechaux, National Research Council, National Materials Advisory Board, 2101 Constitution Ave. NW, Washington, DC 20418 USA

2:00 PM Opening Remarks

2:10 PM Invited
Why Did the World Trade Center Collapse? Science, Engineering, and Speculation: *Christopher Musso*[1]; Thomas W. Eagar[1]; [1]Massachusetts Institute of Technology, Matls. Sci. & Eng., 77 Massachusetts Ave., Cambridge, MA 02139 USA

There have been numerous reports detailing the cause of the World Trade Center collapse on September 11, 2001. Most have provided qualitative explanations; however, simple quantitative analyses show that some common conclusions are incorrect. For example, steel could not have melted in the Tower fires and there was more stuctural damage than simple softening of the steel at elevated temperatures. Some guidelines for improvements in future structures are also presented.

2:50 PM Invited
New Materials for Building Structures?: *John Hooper*[1]; [1]Skilling Ward Magnusson Barkshire, 1301 Fifth Ave., #3200, Seattle, WA 98101-2699 USA

Although new materials are being introduced into the building structures, their introduction is slowed by many factors including costs and the code approval process. Our "new materials", generally, relate to finding new ways to use familiar materials. Advances in analysis tools and methodologies has allowed this opportunity to extend the envelope and geometric application of traditional materials such as steel, timber and concrete as well as developing new concepts for nonstructural items such as curtain walls and stairs. Applications of these advances will be presented with additional discussion regarding the next generation provided. Research is underway that, over time, will allow for carbon, kevlar, mylar and other composites to enter building structure mainstream. Some examples of these opportunities will be presented and estimated time table regarding their use given.

3:30 PM Break

3:40 PM Invited
A Structural Engineer's Dream for Ideal Post 9/11 Construction Materials: Loring A. Wyllie[1]; [1]Degenkolb Engineers, 225 Bush St., Suite 100, San Francisco, CA 94104-4207 USA

A Structural Engineer uses existing construction materials to design many large complex structures to provide safety to its occupants. Connections must be adequate and designs consider some extraordinary conditions such as strong winds and earthquakes. With the recent wave of terrorist attacks there is a desire to toughen our structures to improve their performance under extreme and unexpected loadings. While some improved structural details will help, better materials would significantly improve performance for these unexpected conditions. The talk will focus on some of the material properties that Structural Engineers would consider ideal for survival under extreme conditions. Normally, material changes are relatively minor and focus on higher strength, improved chemistry to facilitate connections or improved ductility. Rather than trying to make minor changes to existing materials, the talk will step back and dream of new materials that would significantly improve our built environment for the unexpected loadings and conditions which may occur.

4:20 PM Invited
Virtual Materials and Service Life Design: *Geoffrey Frohnsdorff*[1]*;* Ken P. Chong[2] [1]National Institute of Standards and Technology, Guest Researchers, Building and Fire Research Lab., Rm. B368, Bldg. 226, Gaithersburg, MD 20899 USA; [2](On leave from the National Science Foundation)

The designer of a building, or other constructed asset, must exercise many judgments in ensuring that the intended life will be achieved without large unforeseen expenses. The generally-satisfactory performance of buildings attests to the generally-good judgment of designers. However, enough durability problems occur to suggest that more needs to be done to help ensure achievement of the intended service life at a reasonable life-cycle cost. Possibilities for increasing the likelihood of satisfactory long-term performance are: 1) establishing service life design standards, 2) providing reliable and realistic accelerated tests and models for predicting long-term behavior of materials and components, and 3) providing convenient access to reliable, easily-usable knowledge about the long-term performance of materials and components.

Materials Processing Fundamentals - IV

Sponsored by: Extraction & Processing Division, Process Fundamentals Committee
Program Organizers: P. N. Anyalebechi, Grand Valley State University, Padnos School of Engineering, Grand Rapids, MI 49504-6495 USA; Adam Powell, Massachusetts Institute of Technology, Cambridge, MA 02139-4301 USA

Wednesday PM — Room: 614
February 20, 2002 — Location: Washington State Conv. & Trade Center

Session Chairs: Alvaro Giron, Alcoa Technical Center, Ingot & Solidification Platform, 100 Technical Dr., Alcoa Center, PA 15069 USA; Adam Powell, Massachusetts Institute of Technology, 17 Massachusetts Ave., Rm. 4-117, Cambridge, MA 02139-4301 USA

2:00 PM
Applications of High Frequency Induction Heating for Metallurgical Simulation and Thermal Analysis of Industrial Light Metals Casting Processes: *W. Kasprzak*[1]; W. T. Kierkus[1]; J. H. Sokolowski[1]; M. Kasprzak[2]; [1]NSERC/Ford-Nemak/University of Windsor, Mech., Autom. & Matls. Eng., Rm. 203, Essex Hall, 401 Sunset Ave., Windsor, Ontario N9B 3P4 Canada; [2]Silesian University of Technology, B. Krzywoustego St. No. 2, Gliwice 44-100 Poland

Modern light metals processing technologies are very complex and involve a diverse set of variables that must be quantitatively evaluated. The most effective way to design new casting processes that deliver specified metallurgical and mechanical properties is to develop a method of simulating the real time process within a test sample of sufficient size. The results can then be analyzed and required optimizations can be performed. This paper presents a novel method of simulating the industrial casting processes in a laboratory environment using experimental apparatus based on the principle of high frequency induction heating. The applicability and accuracy of the proposed analytical method is demonstrated, as an example, by simulation of the solidification and heat treatment of a test sample composed of two dissimilar materials. The simulation can be used to develop a stress model for an automotive component made from an aluminum based alloy with iron cylinder liner inserts.

2:30 PM
Unsteady Mold Flow Analysis in Continuous and Direct Chill Casting Processes using Large Eddy Simulation: *Anirudh Mukhopadhyay*[1]; [1]Fluent, Inc., 10 Cavendish Ct., Lebanon, NH USA

Traditional design process of the Submerged Entry Nozzles (SEN) in Continuous Casting (CC) of steel and Direct Chill (DC) casting of aluminum often involves scaled water modeling to identify time average and unsteady flow features. Using Computational Fluid Dynamics along with the advanced turbulence model, Large Eddy Simulation (LES), transient mold flow analysis has been carried out. Results are compared with the experimental results of Xu et al (1998)*. These simulations showcase both time-averaged and transient flow features along with the effects of variation of port angles. Use of LES makes the quantitative assessment of turbulence more practical with transient and anisotropic large-scale vortical structures within the molds. This study illustrates the utility of CFD in optimizing the analysis effort by reducing the extent of water model experiments and plant trails. *D. Xu, W. K. Jones Jr., J. W. Evans and D. P. Cook, 1998, Applied Mathematical Modeling, vol. 22, pp. 883-893.

3:00 PM
Kinetics of Alumina Dissolution in Molten Slags: *Weol D. Cho*[1]; Peter Fan[1]; [1]University of Utah, Metlgcl. Eng., 135 S. 1460 E., Rm. 412, Salt Lake City, UT 84112 USA

Fast dissolution of nonmetallic inclusions such as alumina particles in molten slags has been required in secondary steelmaking)ladle and tundish)to minimize the amount and the size of nonmetallic inclusions in steel products. In the present work, the dissolution behavior of alumina particles in molten CaO-Al2O3 and CaO-Al2O3-SiO2 slags at the temperatures between 1450 and 1550°C have been investigated in terms of kinetics and mechanism. Alumina particles were added directly into the slags and the variation of the particle size with time was determined using optical and electron microscopies. The conventional types of slag for ladle and tundish were included in the dissolution study. The effects of Al2O3, SiO2, CaF2 and MgO contents on the dissolution rate of alumina particles have also been determined. The diffusion boundary layer between alumina particle and bulk slag phase has been observed and analyzed using SEM and EDS. Based on the analysis of kinetic data and the boundary layer, the dissolution mechanism has been discussed.

3:30 PM Break

4:00 PM
Kinetics Aspects of Zinc Basic Carbonate Decomposition: *N. Kanari*[1]; D. Mishra[1]; I. Gaballah[1]; B. Dupré[2]; [1]Mineral Processing and Environmental Engineering Team, LEM, CNRS UMR 7569, ENSG, INPL, BP 40, 54501 Vandœuvre France; [2]Laboratoire de Chimie du Solide Minéral, UHP Nancy I, UMR 7555, BP 239, 54506, Vandœuvre France

The thermal decomposition studies of two zinc basic carbonate samples were carried out up to 400°C by thermogravimetric analysis, boat experiments and differential scanning calorimetry measurements. The initial samples and the solid decomposition products were analyzed by scanning electron microscopy, x-ray diffraction and laser particle size analyzer. The thermal decomposition of both samples started at about 150°C and the rate of decomposition became significant at temperatures higher than 200°C. The apparent activation energies ‘Ea’ in the temperature range 150-240°C for sample decomposition were between 132 and 153 kJ/mole depending on the sample origin. The XRD analyses of the intermediately decomposed samples and the DSC results up to 400°C suggested that the decomposition reaction most probably occur in a single step.

Materials & Processes for Submicron Technologies - II: Microstructures, Properties & Characterization

Sponsored by: Electronic, Magnetic & Photonic Materials Division, Thin Films & Interfaces Committee
Program Organizers: Seung H. Kang, Lucent Technologies, Orlando, FL 32819 USA; N. (Ravi) M. Ravindra, New Jersey Institute of Technology, Department of Physics, Newark, NJ 07102-1982 USA

Wednesday PM — Room: 209
February 20, 2002 — Location: Washington State Conv. & Trade Center

Session Chairs: Ashok Kumar, University of South Florida, Ctr. for Microelect. Rsrch.; Sailesh M. Merchant, Agere Systems, VLSI Proc. Dvlp.

2:00 PM
Electrical and Compositional Properties of TaSi2 Films: *Vishal Mehta*[1]; Anthony T. Fiory[1]; [1]New Jersey Institute of Technology, Dept. of Phys., Newark, NJ 07102 USA

Electrical and compositional properties of sputter deposited TaSi2 films, as function of film thickness, is presented in this study. In particular, the effects of annealing of the TaSi2 fillms in steam ambients has been investigated. It is found that the films are very stable and at least within the limits of X-ray diffraction, no observable oxidation of the films has been detected. A comparison of the present study is made with the literature. The evolution of the structure of the films with film thickness is also investigated.

2:20 PM Invited
Process Parameter Impacts on the Properties of Cu Interconnects: *Jon Reid*[1]; John Sukamto[1]; [1]Novellus Systems

The transition from etched Al to electroplated Damascene interconnects is now well underway for the 0.13 micron device generation. The electrodeposition chemistries and process conditions required to achieve uniform within die plated thickness, complete filling of smaller high aspect ratio features, and low metal defect densities have evolved considerably from the chemistries and conditions initially introduced for IC applications. In many cases, the changes in accelerating, suppressing, and leveling additives, electrolyte component concentrations, and electroplating current profiles required to meet criteria such as void free filling have also influenced the metallurgy of the copper deposit. Important interconnect behaviors such as electromigration stability and via chain yield thermal stability are known to depend strongly on barrier properties and initial filling quality. The importance of deposit metallurgy to these behavior and a clear understanding of the electrodeposited metallurgy itself has not been well established. In this paper, deposit properties such as resistivity, stress, purity, void formation, and grain structure are studied at various stages of annealing as a function of deposition current, additive concentration and type, and electrolyte concentrations.

2:50 PM
Plastic Deformation of Electrodeposited Cu Foil at Low Homologous Temperatures: *Hans Conrad*[1]; Di Yang[1]; [1]North Carolina State University, Matls. Sci. & Eng., PO Box 7907, Raleigh, NC 27695-7907 USA

The plastic deformation kinetics of electrodeposited (EP) 18mm Cu (grain size vapor deposited (VP) Cu foil (d=0.5mm) tested at 77-473K. The apparent activation volume v=kTlne/s for both materials exhibited a minimum at ~350K, while the flow stress decreased monotonically. The values of v for the EP Cu foil at e» 0.05 were smaller than those for the EP foil determined at e=0.008. The rate-controlling mechanism in both materials at T< 350K appears to be grain boundary shear induced by dislocation pile-ups, that at T>350K may be either cross slip or dislocation climb controlled by dislocation pipe diffusion.

3:10 PM
Effects of Mechanical and Tribological Properties of Low-K Materials on Chemical Mechanical Polishing: Arun Kumar Sikder[1]; Frank Giglio[1]; John Wood[1]; *Ashok Kumar*[1]; Mark Anthony[1]; [1]University of South Florida, Ctr. for Microelect. Rsrch., Col. of Eng., 4202 E. Fowler Ave., Tampa, FL 33620 USA

In the 50 nm node, the International Roadmap for Semiconductors (ITRS) predicts a need for dielectrics with a bulk K value of <1.3 and effective K value <1.5 for the dielectric stack. Mechanical characterization of low-K materials has shown that lower K typically also means lower elastic modulus and hardness. Also the major challenges involves in chemical mechanical polishing (CMP) of these films due to the reduced modulus and cohesive strength of many low-K materials. In this study, we investigate the mechanical and tribological properties of low-K dielectric materials. The films surface properties along with the mechanical properties affect the within-wafer-nonuniformity, removal rate and roughness. The friction coefficient and acoustic emission signal was monitored during CMP process. The film surfaces were characterized using both SEM and atomic force microscopy. Effect of friction co-efficient, hardness and modulus on the polishing behavior was investigated. The validity of Preston's equation was also discussed.

3:30 PM
Effects of Pad Characteristics on Material Removal Rate in CMP: Bo Yan[2]; *Ashraf Bastawros*[2]; *Abhijit Chandra*[1]; [1]Iowa State University, Mechl. Eng., 3038 Black Eng. Bldg., Ames, IA 50011 USA; [2]Iowa State University, AEEM Dept., Ames, IA 50011 USA

The role of the porous pad in controlling the material removal rate (MRR) during the chemical mechanical planarization (CMP) process has been studied numerically. The numerical results are used to develop a phenomenological model that correlates the forces on each individual polishing particles to the applied nominal pressure. The model provides physical explanation of experimentally observed domains of pressure dependent material removal rates, wherein the pad deformation controls the load sharing between active cutting particles and direct wafer-pad contact. The predicted correlations between MRR and slurry characteristics (i.e., particle size, concentration) are in agreement with experimentally measured trends.

3:50 PM Break

4:10 PM Invited
Characterization and Optimization of Copper CMP Planarization: *Thomas Laursen*[1]; Tezer Battal[1]; Ben Palmer[1]; Malcolm Grief[1]; [1]SpeedFam-IPEC

Abstract unavailable

4:40 PM
Experimental and Numerical Analyses on Mechanical Stress Evolution in Metal Interconnects for Various Line Aspect Ratios and Passivation Dielectrics: *Young Bae Park*[1]; In Soo Jeon[1]; Hyuk Hyun Ryu[1]; Won Gyu Lee[1]; [1]Hynix Semiconductor, Inc., Adv. Logic Proc. Dvlp. Team, Sys. IC R&D Div., 1 Hyangjeong-dong Hungduk-gu, Cheongju-si 361-725 Korea

Mechanical stress in metal interconnect line is very important in large scale device integration because the metal line is mostly under a tri-axial tensile stress state that is favorable for void formation which is a major concern for the reliability of multi-level metallization. Both direct X-ray diffraction analysis and finite element analysis were used to investigate the effects of various passivation dielectrics and metal line aspect ratios on the mechanical stress-state in Al-Cu interconnect lines. Passivation dielectrics used in this study were PETEOS (Plasma Enhanced Tetra Ethyl Ortho Silicate), FOX (Flowable Oxide), HDP FSG (High Density Plasma Fluorinated Silicate Glass), and SiN (Silicon Nitride). A series of parallel interconnect lines with various aspect ratios (or, various line widths of 0.25 ~ 10µm at a constant thickness) and a constant pattern density of 50% were used for stress analysis. Plane-strain, elasto-plastic finite element analyses were carried out to calculate thermal stress by using Young's modulus of each constituent layer measured with nanoindentation method. Finally, average thermal stresses from finite element analysis were compared to experimentally measured estimates by considering not only residual stresses and mechanical properties of passivation dielectrics but also their characteristic deposition shapes.

5:00 PM
Improvement of Form Accuracy in Hybrid Machining of Microstructure: *Lim Han Seok*[1]; A. Senthilkumar[1]; M. Rahman[1]; [1]National University of Singapore, Dept. of Mechl. Eng., 10, Kent Ridge Crescent 119620 Singapore

Micro machining is gaining popularity due to the recent advancements in Micro Electro Mechanical Systems. Using conventional micro machining it is relatively difficult to produce moving components in the order of microns. Therefore an attempt is made in this paper to build microstructures using a combination of turning and electrochemical machining. Several sets of experiments were performed to study the characteristics of the hybrid machining process. From the experiments it was observed that higher form accuracy could be obtained by integrating the on machine fabrication of machining tool and subsequently using the tool for machining the workpiece. The main cause of the form error is due to the deflection of the shaft while machining and hence an attempt was made to develop the deflection sensor. The deflection error was observed using the developed sensor and it was compensated using the feedback mechanism thus considerably improving the form accuracy of the component. The procedure involved and the results obtained are discussed in detail in this paper.

5:15 PM
A Study on the Grinding of Glass using Electrolytic Inprocess Dressing: *A. Senthilkumar*[1]; M. Rahman[1]; Lim Han Seok[1]; K. Fathima[1]; [1]National University of Singapore, Dept. of Mechl. Eng., 10, Kent Ridge Crescent 119620 Singapore

Grinding of brittle materials like glass is gaining importance due to the rapid development in the areas such as machining of storage devices, micro lenses and optical communication devices. Grinding of such glasses are difficult due to their brittle nature and the grinding wheel worn out easily due to the hardness of the material being machined. Therefore an electrolytic in process dressing (ELID) of the grinding wheel is used to dress the wheel continuously so as to make the fresh diamond grit to protrude and grind the glass under ductile mode machining in order to yield surface roughness in the order of nanometers. In this paper a fundamental study on the mechanism of ELID grinding technique is discussed in detail. Several sets of experiments were performed to determine the optimal grinding conditions. From the experiments it was observed that surface roughness could be improved if the current duty ratio to dress the grinding wheel is increased. The force patterns and the changes in the profile of the grinding wheel are presented and discussed in detail.

Modeling of Multi-Scale Phenomena in Materials Processing: Process Analysis

Sponsored by: ASM International: Materials Science Critical Technology Sector, Materials Processing & Manufacturing Division, Jt. Computational Materials Science & Engineering, Solidification Committee

Program Organizers: Adrian Sabau, Oak Ridge National Laboratory, MS-602, Oak Ridge, TN 37831-6083 USA; Boyd A. Mueller, Howmet Corporation, Whitehall, MI 49461-1832 USA; Anthony D. Rollett, Carnegie Mellon University, Department of Materials Science & Engineering, Pittsburgh, PA 15213-2890 USA

Wednesday PM — Room: 304
February 20, 2002 — Location: Washington State Conv. & Trade Center

Session Chair: Adrian S. Sabau, Oak Ridge National Laboratory, Metals & Cer., Bethel Valley Rd., Bldg. 4508, MS 6083, Oak Ridge, TN 37831 USA

2:00 PM

Simulation of Fine Particle Dynamics in Materials Processing Systems: *Aniruddha Mukhopadhyay*[1]; Abhijit Dutta[1]; Eric William Grald[1]; Evan Whitby[2]; Frank Stratmann[2]; Martin Wilck[2]; [1]Fluent, Inc., 10 Cavendish Ct., Lebanon, NH 03766 USA; [2]Chimera Technologies, Inc., 15051 Zodiac St. N.E., Forest Lake, MN 55025 USA

In many industrial processes particles are either a desired product, such as TiO2 powder, or an unwanted contaminant, such as large particles in chemical vapor deposition reactors. Successful development of such systems requires understanding and controlling processes governing particle formation, growth, transport, and deposition. These processes can be simulated with computational fluid dynamics (CFD) based particle dynamics models. Because no general-purpose, commercial software exists for such particle-dynamics simulations, Chimera Technologies and Fluent are developing the Fine Particle Model (FPM), which is a CFD-based Eulerian model that solves for coupled fluid flow, heat transfer, chemical reactions, and particle dynamics. Typical applications include nano-particle sprays, chemical reactors, pollution formation/transport, and particle inhalation/transport. In this talk we describe processes simulated with the FPM and show typical examples.

2:25 PM

Characterization of Embedded Fiber Optical Sensors: Jill Noel Johnsen[1]; Joanna R. Groza[1]; Fritz Prinz[2]; Xiaochun Li[2]; [1]University of California, Chem. Eng. & Matl. Sci., One Shields Ave., Davis, CA 95616 USA; [2]Stanford University, Palo Alto, CA USA

The benefit of Laser Assisted Shape Deposition Manufacturing (LASDM) and other rapid prototyping processes is the ability to create physical models with little or no restriction from shape complexity. Silica fibers have been embedded into real parts to be used as in-situ sensors for stress and temperature measurements during their operation. The parts produced and characterized for this study consist of layers of stainless steel, nickel, and fibers. First, a layer of nickel was electrolytically deposited on a stainless steel support. Then fibers, which were sputter coated with a thin metal film, were placed on this layer of nickel and topped with another layer of electrolytically deposited nickel, followed by a stainless steel deposit by LASDM. The deposited stainless steel was created with a 20 mm/s velocity, a 2000 W laser power, and a 20 g/min deposition rate. Microstructural studies of each layer and interfaces were conducted using SEM and optical microscopy. The nickel grain structure was found to be very uniform around the fibers both before and after laser deposition and the fibers showed good adhesion to the matrix. In situ stress and temperature measurements were successfully performed on fiber embedded parts to test the validity of this approach.

2:50 PM

Evaluation of Field Activated Sintering of Silicon: *Martin Kramer*[1]; Joanna R. Groza[1]; [1]University of California, Matls. Sci. Dept., Davis, CA 95616 USA

A kinetic study on sintering pure, fine grained silicon powder by field activated sintering using the Sumitomo SPS sintering system has been carried out. Densities better than 97% could be achieved by tailoring temperature and pressure profiles. Densification kinetics as a function of different heating rates and uniaxial pressures have been determined to derive experimental values for activation energies. The results are discussed in terms of kinetics and the technical capabilities and potential of the sintering system addressing both problems of temperature distribution throughout the specimen and furnace setup which have been studied by finite element modeling and experiments.

3:15 PM Break

3:30 PM

Assessment of Diffusion between Nickel Base Superalloys: Rob Marsh[1]; *Carelyn E. Campbell*[2]; Ty W. Hansen[1]; Boyd A. Mueller[1]; William J. Boettinger[2]; [1]Howmet Research Corporation, Elect. Prod. Tech., 1500 S. Warner St., Whitehall, MI 49461 USA; [2]National Institute of Standards, Metall. Div., Gaithersburg, MD 20899 USA

The availability of thermodynamic databases for up to 15 components developed through the Calphad approach has permitted the prediction of solidification path in commercial superalloys. The enthalpy and the derived density information predicted for these paths has been employed in the modeling of macroscopic heat transfer and fluid flow phenomena in real parts. An area that has received considerably less attention is the solid state diffusion processes which occur during heat treatment and coating operations. This presentation will report on experimental diffusion couple studies for a series of times between various nickel base superalloys such as Rene N4 and Rene N5 at temperatures in the single phase gamma' region. The couples were analyzed by microprobe to map the extent of diffusion. The experimental results are compared to numerical predictions of the code DICTRA using the available thermodynamic database and a mobility database assessed from diffusion data in the various binary and ternary subsystems.

3:55 PM

Brownian Dynamic Simulation of the Rheology of Dense Colloids: *Andrew Martin Mullis*[1]; [1]University of Leeds, Dept. of Matls., Clarendon Rd., Leeds, W. Yorkshire LS2 9JT UK

Dense colloidal suspensions are structured fluids displaying complex rheological properties, including both shear thinning and shear thickening. One route to understanding such systems is Brownian Dynamics, a particle dynamics technique in which hydrodynamic interactions between the particles are ignored. Simulations containing thousands of particles are feasible, yielding statistical information about the level of structure in the fluid. Brownian Dynamics thus spans several length scales relating interparticle forces to the suspension microstructure and hence the rheology of the bulk slurry. We will give an overview of the technique illustrated by simulations of a dense (55% volume fraction solid) suspension of repulsively electrostabilized particles. Such suspension are observed to undergo a shear thickening transition with increasing applied shear, related to an order-disorder transition in the microstructure. This sequence is reproduced in the simulations with progressive loss of order being observed as the applied shear is increased.

4:20 PM

Multi-Scale Modeling of Packed Bed: *Subrata Pal*[1]; A. K. Lahiri[1]; [1]Indian Institute of Science, Dept. of Metall., Bangalore 560 012 India

The modeling studies of the counter current gas-solid reactors are usually done assuming all solids as continuum. In this approach the transport processes occurring in the individual particle are neglected. A multi-scale model of char burning in a moving bed has been carried out. The temperature profile in the char bed as well as in the char particle has been computed considering all the possible reactions. Cylindrical and spherical coordinate systems have been used for the reactor and the particle respectively.

Phase Stability, Phase Transformations & Reactive Phase Formation in Electronic Materials - III

Sponsored by: Electronic, Magnetic & Photonic Materials Division, Structural Materials Division, Alloy Phases Committee
Program Organizers: Sinn-Wen Chen, National Tsing-Hua University, Department of Chemical Engineering, Hsinchu City 300 Taiwan; C. Robert Kao, National Central University, Department of Chemical Engineering, Chungli City, Taiwan; Hyuck Mo Lee, Korea Advanced Institute of Science & Technology, Department of Materials Science & Engineering, Taejon 305-701 Korea; Michael R. Notis, Lehigh University, Department of Materials Science, Bethlehem, PA 18015 USA; Douglas J. Swenson, Michigan Technological University, Department of Metallurgical & Materials Engineering, Houghton, MI 49931 USA

Wednesday PM	Room: 211
February 20, 2002	Location: Washington State Conv. & Trade Center

Session Chairs: Michael R. Notis, Lehigh University, Dept. of Matls. Sci. & Eng., 442 Whitaker Lab., Bethlehem, PA 18015 USA; C. Robert Kao, National Central University, Dept. of Cheml. & Matls. Eng., Chung-li, Taiwan

2:00 PM Invited
Ripening-Controlled Solder Interfacial Reactions: *King-Ning Tu*[1]; [1]UCLA, Matls. Sci. & Eng., 6532 Boelter Hall, Los Angeles, CA 90095-1595 USA

Kinetic models of reactive phase formation with planar interfaces in solid state reactions are well established. Whether they are diffusion-controlled or interfacial-reaction-controlled models, no surface and interfacial energies are taken into account. In solid state aging of a solid solder (e.g., eutectic SnPb) on a solid conductor (e.g., Cu), the intermetallic compound (IMC) formed between them has a layer-type morphology. But in the wetting reaction between molten solder and a solid conductor, the IMC formed between them has a scallop-type morphology. The interface of the scallops is non-planar and the growth of an average size scallop has been found to show t 1/3 dependence, suggesting that it may be controlled by ripening. The growth rate of scallop-type IMC is four orders of magnitude faster than that of the layer-type. To develop a kinetic model of ripening-controlled interfacial reactions, we have confirmed that the scallop-type morphology is thermodynamically stable in the wetting reaction, because of minimization of interfacial and grain boundary energies. Among the kinetic processes in the growth of scallops, the growth itself or ripening becomes the slowest step because the scallops are 3-dimensional. We propose that the interfacial reaction is ripening-controlled.

2:25 PM Invited
Morphology and Growth Kinetics of Solder/Substrate Interfacial Reaction Products using Tin-Based Solders: *Michael R. Notis*[1]; Sarah L. Allen[1]; Ben K. Jackson[1]; Rick P. Vinci[1]; [1]Lehigh University, Matls. Sci. & Eng., 442 Whitaker Lab., Bethlehem, PA 18015 USA

The nature and kinetics of growth of interfacial reaction products that form during soldering using lead-free tin-based alloys on copper substrates is of significant concern for the manufacture of many commercial electronic component and package configurations. This paper will first review the literature and our own studies concerning the morphology and kinetics of growth of interfacial reaction products in liquid-solid and solid-solid tin/copper diffusion couples. These results will be compared with growth studies involving silver-tin binary and silver-copper-tin ternary solders on copper substrates. In the silver-containing solders, long needle-like growths of Ag3Sn appear to nucleate and grow into the solder from the interfacial region. We have used a deep-etching method to examine the nucleation and growth morphology of this Ag3Sn phase. Suggestions as to the reasons for rapid anisotropic phase growth will be made, and possible effects on mechanical properties will be discussed.

2:50 PM Invited
Strong Effect of Cu Concentration on the Reactions between SnAgCu Lead-Free Solders and Ni: C. E. Ho[1]; *C. Robert Kao*[1]; [1]National Central University, Dept. of Cheml. & Matls. Eng., Chungli City Taiwan

The electronic industry recently reached a consensus that the 95.5Sn-3.9Ag-0.6Cu (wt.%, Sn-3.9Ag-0.6Cu) was the most promising lead-free candidate to replace the lead-bearing solders. In this study, the effect of a small perturbation in Cu concentration was studied. Specifically, two solders, Sn-3.9Ag-0.2Cu and Sn-3.9Ag-0.6Cu, were reacted with Ni at 250°C. It was found that the Cu concentration had a strong effect on the reaction. When Sn-3.9Ag-0.2Cu was reacted with Ni, a continuous $(Ni_{1-x}Cu_x)_3Sn_4$ intermetallic layer formed at the interface. When Sn-3.9Ag-0.6Cu was reacted with Ni, a continuous $(Cu_{1-y}Ni_y)_6Sn_5$ intermetallic layer formed at the interface. These two intermetallic compounds might produce solder joints with very different strength. The results of this study shows that the industry must impose a very strict control over the Cu concentration in order to produce the desired intermetallic compound that has the right mechanical properties.

3:15 PM Invited
Mechanisms of Channel Formation and its Effects on Kinetics of Intermetallic Layer Growth at Solder/UBM Interface: Jong-Hyun Lee[1]; Jong-Hwan Park[1]; *Yong-Seog Kim*[1]; [1]Hong-Ik University, Matls. Sci. & Eng., 72-1 Sangsu Dong, Seoul 121-791 S. Korea

Mechanisms of channel formation at solder/UBM interface were investigated by studying orientation of scallop formed at the interface and penetration behavior solders into intermetallics such as Cu6Sn5 and Ni3Sn4. Orientation of scallops analyzed by EBSD technique indicated that the scallops grow in a preferred direction and their grain boundaries are of high angle in character. The penetration speed of solders into the intermetallic, especially the Cu6Sn5, was measured to be orders of magnitude faster than the growth rate of the intermetallics during reflow soldering. These results indicate that the channels at solder/UBM interface are thermodynamically stable throughout the reflow soldering process and formed by wetting of solders into the grain boundaries of intermetallics. The effects of channel presence on the growth kinetics of intermetallics at solder/UBM interface were analyzed theoretically and measured experimentally.

3:40 PM Break

4:00 PM Invited
Prediction of Primary Intermetallic Compound Formation during Interfacial Reaction between Sn-Based Solder and Ni Substrate: Won Kyoung Choi[2]; *Hyuck Mo Lee*[1]; Sang Won Jeong[1]; [1]KAIST, Dept. of Matl. Sci. & Eng., Kusung-Dong 373-1, Yusung-Gu, Taejon Korea; [2]IBM Watson Research Laboratory, PO Box 218, Yorktown Heights, NY 10598 USA

A modified methodology to predict the primary intermetallic compound (IMC, hereafter) phase that forms first during soldering at the interface between Sn-based solders and metal surfaces is suggested. By comparing the activation energy for nucleation of individual IMC phases, which is a function of the interfacial energy and the driving force for formation, the IMC phase that forms first is predicted as the one with the smallest activation energy. This methodology has been successfully applied to observations of IMC phases that form during liquid soldering on Cu and Ni plates.

4:25 PM Invited
Variation of Melting Temperature upon Particle Size Reduction: *Kwang-Lung Lin*[1]; [1]National Cheng Kung University, Matls. Sci. & Eng., 1 Ta-Hsuey Rd., Tainan 701 Taiwan

Solder paste applies solder powder for forming microelectronic interconnection. Pb-free solder development generally attempts to search for eutectic system in order to lower the reflow temperature. It however has been known that the melting temperature of a material can be lowered by particle size reduction. This present work performed an analysis on the behavior of melting temperature depression, basing on classical thermodynamic theory, for several metals. It is shown that there exists a particle diameter, termed as critical radius of fusion, at which the latent heat of fusion of a fixed mass equals the total surface energy of the particles. It was found that this radius is in the range of nano-size. The depression of melting temperature also becomes quite prominent in the range of nano-size. This suggests a possibility of performing solder reflow at lower temperature than the melting temperature of the bulk solder.

4:50 PM Invited
Two Phase Equilibrium in Electronic Materials and its Application in Advanced Devices: *Choong-Un Kim*[1]; ManJong Lee[1]; Nancy Michael[1]; Qing-Tang Jiang[2]; [1]The University of Texas at Arlington, Matls. Sci. & Eng., Woolf Hall, Rm. 325C, Arlington, TX 76019-0031 USA; [2]International Sematech, Austin, TX 78741-6499 USA

The proximity to equilibrium is important to all material systems, including electronic devices. Equilibrium seeking behavior can be exploited to develop new classes of electronic materials or it can drive damage mechanisms. This paper will present two examples of materials designed to actively use two-phase equilibrium and one example of device damage resulting from interface instability. The first example is the use of solid-solid phase equilibrium to efficiently develop semiconductor quantum-dots. Semiconductor alloys with limited mutual solubility, for example PbTe-4HgTe, can be processed to induce precipitation in a controlled manner. The resulting nanocrystals are self-assembled and self-aligned. The second example is the use of low-temperature solder alloys in a solid-liquid equilibrium state as a thermal interface material. In the two-phase state, the alloy reduces thermal resistance far better than any existing contact material. Finally, the role of solid-gas equilibrium during electromigration failure of submicron Cu interconnects will be introduced.

Second International Symposium on Ultrafine Grained Materials: Mechanical Behavior

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

Program Organizers: Yuntian Ted Zhu, Los Alamos National Laboratory, Materials Science and Technology Division, Los Alamos, NM 87545 USA; Terence G. Langdon, University of Southern California, Department of Mechanical Engineering, Los Angeles, CA 90089-1453 USA; Terry C. Lowe, Technanogy, Newport Beach, CA 92627 USA; Rajiv S. Mishra, University of Missouri, Metallurgical Engineering, Rolla, MO 65409-0340 USA; Michael Jeremi Saran, Case Western Reserve University, Cleveland, OH 44106 USA; S. Lee Semiatin, Air Force Research Laboratory, Materials & Manufacturing Directorate, WPAFB, OH 45433 USA

Wednesday PM	Room: 210
February 20, 2002	Location: Washington State Conv. & Trade Center

Session Chairs: Amiya K. Mukherjee, University of California, Dept. of Chem. Eng. & Matls. Sci., Davis, CA 95616 USA; Evan Ma, Johns Hopkins University, Dept. Matls. Sci. & Eng., 105 Maryland Hall, 3400 N. Charles St., Baltimore, MD 21218 USA

2:00 PM Keynote

Dislocation Activity in Nanocrystalline Model Metals: Richard C. Hugo[2]; Harriet H. Kung[2]; *Julia R. Weertman*[1]; [1]Northwestern University, Matls. Sci. & Eng., Evanston, IL 60208 USA; [2]Los Alamos National Laboratory, Matls. Sci. & Tech., Los Alamos, NM 87545 USA

The deformation behavior of nanocrystalline metals at very small grain sizes (<~20 nm) has been the subject of experiments, theories, and molecular dynamics simulations. It has been predicted that dislocation activity ceases and grain boundary sliding becomes dominant at the ultrafine grain sizes. Results of these studies will be reviewed and recent experiments described of in situ straining in the TEM of Ni nanocrystalline films to look for dislocation activity. This research was partially supported by the Department of Energy's Office of Basic Energy Research and by the LDRD program at the Los Alamos National Laboratory.

2:25 PM Invited

Current Views on the Fatigue Performance of Ultrafine-Grained Metals: *Hael Mughrabi*[1]; Heinz Werner Hoeppel[1]; [1]University Erlangen-Nuernberg, Inst. fuer Werkstoffwissenschaften, Martensstr. 5, Erlangen D-91058 Germany

The most important factors that control the cyclic deformation behaviour and fatigue life of ultrafine-grained (UFG) materials have become clearer in recent time. Interesting aspects of the earlier work were that the strength enhancement related to the strongly reduced grain size, paired with an enhanced strength and a reduced ductility, led to an improved fatigue resistance in Wöhler (S-N) plots but to reduced fatigue lives in Manson-Coffin plots. In addition, the mode of testing (stress or strain control) plays a role. The microstructural origin of fatigue damage was identified as macroscopic shear banding in combination with dynamic grain coarsening of the highly meta- or unstable deformed microstructure. Dynamic grain coarsening can obviously occur in UFG materials at homologous temperatures as low as 0.2. Application of a suitable annealing treatment has been shown to improve the stability of the UFG microstructure and to lead to an enhancement of the fatigue performance in the entire range in S-N and in Manson-Coffin plots. These aspects of fatigue of UFG materials are reviewed with reference to the potential of enhancing the fatigue performance of commercial engineering materials.

2:45 PM

Corrosion Fatigue of Ultra-Fine Grain Copper Fabricated by Severe Plastic Deformation: *Hiroyuki Miyamoto*[1]; Takashi Yamasaki[1]; Takuro Mimaki[1]; Alexei Vinogradov[2]; Satoshi Hashimoto[2]; [1]Doshisha University, Mech. Eng., 1-3 Miyakodani Tatara, Kyotanabe, Kyoto 610-0321 Japan; [2]Osaka City University, Dept. Intelligent Matls. Eng., Osaka 558-8585 Japan

Corrosion fatigue is investigated of ultra-fine grain (UFG) copper fabricated by severe plastic deformation through equal-channel angular pressing (ECAP). The corrosion fatigue behaviour in 1M NaNO2 aqueous solution is compared with results of testing in air under low-cyclic regimes with constant plastic strain amplitudes Depl/2 ranged from 2x10-3 to 5x10-2. The significant enhancement of fatigue life in the UFG state is achieved in comparison with polycrystalline copper of ordinary grain size. It is shown that a higher overall resistance against corrosion fatigue can be obtained after grain reduction via ECAP. Detailed structural and morphological investigations are performed on different stages of cycling. While transgranular crack nucleation occurs in ordinary polycrystals, the intergarnular fracture occurs in the UFG material. It is shown that cyclic softening which occurs both in air and in aggressive environment is associated with abnormal grain growth. Formation of a dislocation structure characteristic for persistent slip bands (PSBs) is observed evidently in the grains coarsened during fatigue. The PSB-grain boundary interaction is supposed to facilitate strongly the intergranular fatigue fracture which is particularly pronounced in corrosion fatigue studies where the grain boundaries are preferentially attacked by aggressive spices. The findings of the present investigations are discussed in light of former fatigue experiments performed on ultra-fine grained copper and results of general corrosion stress-corrosion tests. The mechanism of intergranular corrosion fatigue damage in the UFG copper is proposed in terms of corrosion-deformation interactions.

3:00 PM

Texture and Elastic Strain Development during Mechanical Loading of Equal Angle Channel Processed Nickel and Aluminum: *Bjorn Clausen*[1]; Sven Vogel[2]; Ersan Üstündag[1]; Cheng Xu[3]; Donald W. Brown[2]; Mark A.M. Bourke[2]; Terence G. Langdon[3]; [1]California Institute of Technology, Matls. Sci., 1200 E. California Blvd., MC 138-78, Pasadena, CA 91125 USA; [2]Los Alamos National Laboratory, Matls. Sci. & Tech. 8, PO Box 1663, MS H805, Los Alamos, NM 87545 USA; [3]University of Southern California, Dept. of Aeros. & Mech. Eng. & Matls. Sci., 854 W 36th Place, Los Angeles, CA 90089-1453 USA

Severe plastic deformation (SPD) methods allow producing nanostructured metals and alloys. SPD processed metals and alloys can have very high yield strength while high ductility is maintained, a unique and extremely attractive combination of properties. Among other SPD methods, equal-channel angular processing/pressing (ECAP) is an efficient method of refining grain size of metals or composites to the order of 100 nm via severe plastic deformation. We will present results of neutron diffraction measurements investigating texture, grain size and residual strains as a function of ECAP cycles. By the very nature of neutron diffraction experiments, these results are averaged over the bulk of the sample. Additionally, the in-situ measured hkl-dependent response on uniaxial loading of ECAP'ed samples will be shown. The neutron diffraction results will be compared with findings from a self-consistent modeling approach, which will be applied to ultrafine-grained materials for the first time.

3:15 PM

Dry Sliding Wear Behavior of Ultrafine Grained Commercial Purity Aluminum and Low Carbon Steel Produced by Severe Plastic Deformation Techniques: *Yong-Suk Kim*[1]; Taio Lee[1]; Kyung-Tae Park[2]; Woo-Jin Kim[3]; Dong Hyuk Shin[4]; [1]Kookmin University, Sch. of Metlgcl. & Matls. Eng., 861-1 Chonung-dong Songbuk-ku, Seoul 136-702 S. Korea; [2]Hanbat National University, Div. of Adv. Matls. Sci. & Eng., Taejon 300-717 S. Korea; [3]Hong-Ik University, Dept. of Metall. & Matls. Sci., Seoul 121-791 S. Korea; [4]Hanyang University, Dept. of Metall. & Matls. Sci., Ansan, Kyunggi-Do 425-791 S. Korea

Dry sliding wear behavior of ultrafine grained commercial purity aluminum (1100) and low carbon steel (Fe-0.15%C-0.25%Si-1.1%Mn) was investigated. The ultra fine grains of the aluminum and the steel were obtained by an accumulative roll bonding (ARB) process and equal channel angular processing (ECAP), respectively. Pin-on-disk wear tests of the ultrafine grained specimens were carried out under various applied load and sliding speed conditions using hardened bearing steel as a counterpart material. Contrary to the increase of the hardness and yield strength, wear resistance of the ultra-fine grained aluminum and steel specimens was lower than the large grained as-received ones and the resistance decreased with the increase of the accumulative plastic strain. Worn surfaces and cross-sections of the worn specimens were examined with SEM and TEM to investigate the wear mechanism and to explain the wear behavior of the ultrafine-grained aluminum and steel specimens with the microstructural change at the wearing surface.

3:30 PM
Properties and Microstructure of Alumina-Niobium Nanocomposites made by Novel Processing Methods: *Joshua D. Kuntz*[1]; Julin Wan[1]; Goudong Zhan[1]; Amiya K. Mukherjee[1]; [1]University of California, Dept. of Chem. Eng. & Matls. Sci., One Shields Ave., Davis, CA 95616 USA

Alumina-niobium nanocomposites have been fabricated using high-energy ball-milling and electric field assisted sintering (EFAS) or high pressure sintering (HPS). The 10 volume percent niobium nanocomposites have a fracture toughness of ~ 6 MPa√m with only a marginal decrease in hardness. This is nearly twice as tough as a pressureless sintered composite of the same composition reported in work by Garcia et al [J. of Am. Cer. Soc. 1998; 81:429]. This increase in toughness can be attributed to the novel microstructure in the nanocomposites. The present study shows a metallic phase distribution of ~20 nm particles along with a continuous 3-4 nm layer at the boundaries between alumina grains. This microstructure should lead to toughening by increasing ductility at the crack tip instead of the traditional ligament bridging in the crack wake which is typical of metallic-phase toughened ceramics. This material is based upon work supported by, or in part by, the US Army Research Laboratory and the US Army Research Office under contract/grant number G-DAAD19-00-1-0185.

3:45 PM Break

3:55 PM Invited
Strain Hardening, Strain Rate Sensitivity, and Plastic Instabilities in Nanocrystalline and Ultrafine-Grained Metals: *Evan Ma*[1]; D. Jia[1]; Y. M. Wang[1]; K. T. Ramesh[1]; [1]Johns Hopkins University, Ctr. for Adv. Metals & Cer., 3400 N. Charles St., Baltimore, MD 21218 USA

Fe and Ti with grain sizes in the nanophase to micrometer range have been prepared by severe plastic deformation, either through mechanical milling of powders [1] or ECAP [2]. The deformation behavior of the bulk samples prepared through these routes have been studied using quasi-static as well as high strain rate tests. Our focus is to monitor, as a function of plastic strain, the strain hardening behavior and the strain rate dependence of the flow stress, as well as their effects on the deformation/failure mode, especially uniform deformation versus localization and the tensile necking instability. Our experiments indicate that the nanocrystalline (nc) and ultrafine-grained (UFG) metals appear to lose the mechanisms for defect accumulation inside the grains and hence the capacity for strain hardening. Meanwhile, they tend to exhibit a low strain rate sensitivity (m). As a result, the tendency for plastic instabilities and catastrophic failure is enhanced: (adiabatic) shear banding is promoted in lieu of uniform deformation, and in tension necking instability sets in early [2]. For consolidated Fe, shear banding becomes the dominant mode of deformation from the onset of the plastic deformation [1]. Due to the vulnerability to the localized deformation/failure modes, high-strength nc and UFG materials are very limited in uniform deformation and elongation to failure in tension, or under high-rate conditions, even when they are ductile at conventional grain sizes or in compression tests. Some preliminary results will also be reported on the development of some bcc nc or UFG alloys for military kinetic energy penetrators, where the shear banding mode and self-sharpening capability during high rate deformation are desired. [1] Scripta mater. 42, 73 (2000); Acta mater. in review. [2] Appl. Phys. Lett. July 23 issue (2001).

4:15 PM
Mechanical Properties of Ultrafine Grained Aluminum and Ultra Low Carbon Steel Produced by ARB Process: *Nobuhiro Tsuji*[1]; Yuichiro Koizumi[1]; Yoritoshi Minamino[1]; Yoshihiro Saito[2]; Yoshinori Ito[3]; [1]Osaka University, Dept. of Adaptive Machine Sys., 2-1 Yamadaoka, Suita, Osaka 565-0871 Japan; [2]Osaka University, Dept. of Matls. Sci. & Eng., 2-1 Yamadaoka, Suita, Osaka 565-0871 Japan; [3]Osaka University, 2-1 Yamadaoka, Suita, Osaka 565-0871 Japan

Mechanical properties of aluminum and ultra low carbon steel sheets with various ultrafine grain sizes above 200nm were clarified. 1100 aluminum sheet and IF steel sheet were highly strained up to an equivalent strain of 6.4 by ARB (accumulative roll-bonding) process. The ARB processed sheets were filled with pancake shaped ultrafine grains whose mean thickness is about 200nm. Annealing at various temperatures produced various grain sizes ranging from 200nm to 10 micrometers. The strength of ultrafine grained materials held Hall-Petch relationship with the grain size. However, the Hall-Petch slope of tensile strength was much smaller than that of yield strength, which suggests the decrease in work-hardening with decreasing grain size. Uniform elongation suddenly dropped around the grain size of 1 micro-meter, where tensile strength nearly meets yield strength. The sudden decrease in uniform elongation could be explained by plastic instability. Superior toughness of ultrafine grained steel will be also reported.

4:30 PM
An Evaluation of Homogeneity in Ultrafine-Grained Aluminum Prepared by Equal-Channel Angular Pressing: *Cheng Xu*[1]; Terence G. Langdon[1]; [1]University of Southern California, Dept. of Aeros. & Mech. Eng. & Matls. Sci., Los Angeles, CA 90089-1453 USA

Equal-channel angular pressing (ECAP) is a processing technique capable of producing materials with submicrometer grain sizes. Microhardness tests were conducted to investigate the homogeneity of samples of pure aluminum subjected to ECAP via different processing routes. The results show that the samples achieve homogeneity throughout most of their volume after a single pressing and the homogeneity is further improved with increasing numbers of passes through the ECAP die.

4:45 PM
Mechanical Properties of Nanostructured Low-Carbon Steels Produced by Conventional Cold-Rolling and Annealing of Martensite Starting Microstructure: *Rintaro Ueji*[1]; Nobuhiro Tsuji[1]; Yuichiro Koizumi[1]; Yoritoshi Minamino[1]; Yoshihiro Saito[2]; [1]Osaka University, Dept. of Adaptive Machine Sys., 2-1 Yamadaoka, Suita, Osaka 565-0871 Japan; [2]Osaka University, Dept. of Matls. Sci. & Eng., 2-1 Yamadaoka, Suita, Osaka 565-0871 Japan

The present authors have developed simple thermomechanical processing without intense straining to obtain ultrafine grained bulky steel sheets with both high strength and adequate ductility. Plain low carbon steels (JIS-SS400 and SM490) were austenitized and water-quenched to obtain martensite as starting microstructure. As-quenched sheets were conventionally cold-rolled to a strain of 0.8, and subsequently annealed at temperatures of 673K to 973K. The SS400 sheets annealed at around 823K exhibited the multiphase microstructure composed of ultrafine grained ferrite with grain size of 50-300nm, fine cementite uniformly precipitated, and tempered martensite. Owing to this multiphase structure, the nanostructured sheets had both high strength (710MPa 0.2% offset stress and 870MPa tensile strength) and adequate ductility (9% uniform elongation and 20% total elongation). The nanostructured material impact tested at 103K showed ductile fracture even at this low temperature and the fracture surface revealed very fine dimples.

5:00 PM
Microstructure and Properties of 7475 Aluminum Alloy after Equal-Channel Angular Pressing: *Jingtao Wang*[1]; Cheng Xu[2]; Zheng Zhang[1]; Xicheng Zhao[1]; Lizhong Wang[1]; Terence G. Langdon[2]; [1]Xi'an University of Architecture & Technology, Metlgcl. Eng., Yanta Rd., No. 13, Xi'an 710055 China; [2]University of Southern California, Dept. of Aeros. & Mech. Eng. & Matls. Sci., Los Angeles, CA 90089-1453 USA

Equal-Channel Angular pressing (ECAP) was successfully applied to a 7475 aluminum alloy at temperatures from room temperature to 500°C up to an equivalent true strain of ~12 using routes C or Bc. The grain size was refined to within the range from ~0.3 to 1.9 micrometers by ECAP at these different temperatures. There appears to be a grain refinement limit which is dependent on the ECAP temperature. This paper reports investigations on microstructural characterization and tensile properties of the processed aluminum alloy.

5:15 PM Panel Discussion
Terence G. Langdon, Terry C. Lowe, Ruslan Z. Valiev, Michael J. Zehetbaue

Surface Engineering: Science & Technology II: Advances in Coating Technologies

Sponsored by: Materials Processing & Manufacturing Division, Surface Engineering Committee
Program Organizers: Ashok Kumar, University of South Florida, Department of Mechanical Engineering, Tampa, FL 33620 USA; Yip-Wah Chung, Northwestern University, Department of Materials Science & Engineering, Evanston, IL 60208 USA; Gary L. Doll, The Timken Company, Canton, OH 44706 USA; D. S. Misra, Indian Institute of Technology-Bombay, Department of Physics, Powai, Mumbai 400076 India; John J. Moore, Colorado School of Mines, Department of Metallurgy and Materials Engineering, Golden, CO 80401 USA; Kryoshi Yatsui, Nagoka University of Technology, Nagaoka, Niigata 840-2188 Japan

Wednesday PM	Room: 203
February 20, 2002	Location: Washington State Conv. & Trade Center

Session Chairs: Kiyoshi Yatsui, Nagaoka University of Technology, Nagaoka, Nigata 940-2188 Japan; Y. F. Lu, National University of Singapore 119260 Singapore

2:00 PM
Tribolgy of Oxide Based Matrix Composite Coatings with Lubricant Inclusions: *J. S. Zabinski*[1]; T. Fitz[1]; J. E. Bultman[1]; J. J. Hu[1]; A. A. Voevodin[1]; [1]Air Force Research Laboratory, Wright Patterson AFB, OH 45433-7750 USA

Oxides offer thermal stability and oxidation resistance, but typically exhibit high friction, are brittle, and may create abrasive wear debris. Their limitations can be overcome by controlling microstructure and by creating solid lubricant inclusions in composite structures. Yittria stabilized zirconia and alumina were selected as matrix materials and their microstructure was adjusted to maximize toughness through control of lubricant chemistry and particle size. The lubricants studied were gold, molybdenum disulfide, diamond-like carbon, and cesium oxythiomolybdate. They were selected as inclusions in the oxide matrices to permit low friction and wear resistance across vacuum, moist air, and high temperature environments. Pulsed laser deposition combined with simultaneous magnetron sputtering was used to create composites with 2-10 nm lubricant inclusions. The coatings were tough and exhibited low friction in vacuum, dry nitrogen, and moist air to 650°C. The plasma chemistry and physics required for growth of nanocomposites were identified and the tribology of the coatings is discussed in terms of their chemistry, microstructure, and mechanical properties.

2:25 PM Cancelled
Results of Tensile Cracking Experiments with WC/DLC: *Nekkanty Srikant*

2:40 PM
Development of Cermet Thin Film Coatings: *Brajendra Mishra*[1]; Jinhui Zhou[1]; Frank Kustas[2]; [1]Colorado School of Mines, Metlgcl. Eng., 920 15th St., Golden, CO 80401 USA; [2]Engineered Coatings, Inc., 15422 Winterleaf Ct., Parker, CO 80134 USA

Co-deposited thin films of TiC/W, B4C/Mo and TiC-TiB2/W have been fabricated using magnetron sputtering, under conditions of varied working gas pressures, substrate bias and metal concentrations to develop high fracture toughness in combination with high hardness, good adhesion and enhanced wear-resistance. Coatings have been characterized using scratch adhesion, indentation, and sliding wear tests. Films have exhibited very good adhesion with critical scratch adhesion values from 50-70N, with slightly higher values measured for metal-containing films with an adhesion layer. Observations from Rockwell C Brale indentations to compare relative toughness, suggest that adding a moderate amount (from 20 to 40 atomic percent) of metal to the ceramic coatings reduced the damage diameter around the indentations, and resulted in a less-severe cracking mode (fine radial cracking observed for metal-containing films). This suggests that cermet coatings have higher coating/substrate interfacial toughness than pure ceramic coatings. Nanoindentation of the cermet coatings resulted in hardness values in the range of 20-30 GPa, with higher values for coatings with higher metal content. Reciprocating sliding wear tests were performed on the coatings using a tungsten carbide-cobalt (WC-Co) ball counterface. At a lower initial stress of 1.33 GPa, addition of metal to the carbide matrices resulted in higher wear factors, whereas at a higher initial stress of 1.91 GPa, metal-containing ceramic films had lower wear factors than for the pure ceramic coatings. This behavior suggests a load (or stress) sensitive wear performance. The data will be presented to demonstrate the advantages of metal incorporation in ceramic matrix thin films in applications requiring high tribological performance.

2:55 PM
Tribological and Structural Studies of Diamond-Like-Carbon and Fluorocarbon Thin Films: *Jason W. Goldsmith*[1]; Brajendra Mishra[1]; Eli Sutter[1]; John J. Moore[1]; Mark Crowder[2]; Robert Turner[2]; [1]Colorado School of Mines, ACSEL/MME, 1500 Illinois St., Golden, CO 80401 USA; [2]Maxtor Corporation, 2452 Clover Basin Dr., Longmont, CO 80503 USA

Fluorinated diamond-like carbon thin films have physical properties that may prove beneficial at tribological interfaces. The tribological surfaces of a magnetic recording head and disk are coated with very thin, diamond-like-carbon (DLC) films and the disk has an uppermost coating of a near monolayer of a fluorocarbon polymer. The substitution of one or both of these surfaces with a fluorinated DLC may improve the tribological and surface properties of the head-disk interface. In the present work we have carried out deposition of fluorocarbon films using plasma deposition technique and characterize the surface properties. The chemical composition of the deposited fluorocarbon films has been investigated using Fourier transform infrared spectroscopy, X-ray photoelectron spectroscopy and Raman spectroscopy. The film structure was studied using atomic force microscopy and cross-sectional transmission electron microscopy. The chemical and structural properties of the fluorocarbon films as well as their wear, coefficient of friction, wettability with water, hardness, fracture toughness, index of refraction, dielectric constant, and resistivity were compared to DLC films. The relationship between deposition conditions, structure, and properties is discussed.

3:10 PM
Role of Precursors on the Formation of CN_x Deposited by PE-HF-CVD: *Daniela Dumitriu*[1]; Rosendo Sanjines[1]; *Ayatolah Karimi*[1]; [1]Swiss Federal Institute of Technology Lausanne, Dept. of Phys., Lausanne CH-1015 Switzerland

We prepared CN_x films with N content up to 30 at% using various precursors including ammonia, dimethylamine, 3-amino-1,2,4-triazole, methane, ethene and their halogenated derivatives. Using precursors in which N is directly bonded to C, was found to improve the film properties in terms of N incorporation and hardness. Halogenated precursors increase deposition rate and decrease substrate temperature at which deposition occurs, from 700°C down to 200°C. The level of doping with halogen is below 2 at%. The H content of the film drastically decreases when unsaturated compounds are used. This paper deals with the relationship between the growth mechanisms and films properties.

3:25 PM Invited
Tailored Nanomaterial-Based Hard Coatings on Metal and Polymer Substrates: *Ganesh Skandan*[1]; Amit Singhal[1]; [1]Nanopowder Enterprises, Inc., 120 Centennial Ave., Piscataway, NJ 08854 USA

A great deal of emphasis has been placed recently on developing nanostructured films and coatings on metallic and polymeric substrates to impart improved wear properties. The interest stems from the fact that the mechanical behavior of nanostructured materials appears to be significantly different from its coarse grained counterpart. Our recent work shows that the maximum benefit is achieved when the structure of the coating is a composite of micron and nano scale features, and is suitably tailored for any given application. We have successfully applied this concept to two classes of protective coatings: (1) tungsten carbide-cobalt coatings on metal substrates, wherein the agglomerated powder, used as feedstock material in a high velocity oxy-fuel thermal spray gun, is composed of a mixture of micron and nanoscale WC grains, and (2) optically transparent hard coatings on polycarbonate substrates, wherein the coating is composed of relatively large ceramic particles dispersed in a polymer nanocomposite matrix. The structure and properties of these "multimodal" coatings, as they are now called, will be discussed.

3:50 PM Break

4:05 PM Invited
Ultrananocrystalline Diamond: Synthesis, Properties and Applications: *A. V. Sumant*[1]; O. Auciello[1]; D. M. Gruen[1]; J. A. Carlisle[1]; J. Birrell[1]; N. Moldovan[2]; D. Mancini[2]; D. Ersoy[3]; E. Stach[4]; A. Erdemir[5]; [1]Argonne National Laboratory, Matls. Sci. Div., Argonne, IL USA; [2]Argonne National Laboratory, Experimental Facility Div., Argonne, IL USA; [3]University of Illinois, Dept. of Mechl. Eng., Chicago, IL USA; [4]Lawrence Berkeley Laboratory, Natl. Ctr. for Electron Micros-

copy, Berkeley, CA USA; [5]Argonne National Laboratory, Energy Tech. Div., Argonne, IL USA

Diamond is an ideal material for various applications because of its outstanding physical, chemical, mechanical, and electronic properties. Conventional CVD diamond deposition methods have been explored to produce diamond-based microelectromechanical system (MEMS) devices. However, these methods, based on hydrogen-rich plasma chemistries, result in either coarse-grained pure diamond layers with extremely rough surfaces (≥1 μm rms roughness) or in fine-grained diamond films with a significant amount of intergranular nondiamond carbon (~ 50%), which limits its use to specific applications. At Argonne National Laboratory, we are able to produce phase-pure ultrananocrystalline diamond (UNCD) films grown by microwave plasma CVD using C60-Ar or CH4-Ar plasmas. This technique yields films that have 3-5 nm grain sizes and atomically abrupt grain boundaries. In addition, recent studies on N2 doping have shown that this material can have tunable electrical conductivity from insulating to semimetallic. The work at ANL has demonstrated that UNCD films have unique combined mechanical, tribological electron emission, electronic, electrochemical, and biological compatible properties that make this material applicable to a broad range of multifunctional devices from field emitter cold cathodes to MEMS and biocompatible devices. The synthesis and properties of UNCD films will be reviewed in view of these multiple applications.

4:30 PM

Characteristics of Boron Carbide Films Prepared by Cathodic Arc Deposition: *Othon R. Monteiro*[1]; Marie-Paule Delplancke-Ogletree[2]; C. Christopher Klepper[3]; [1]Lawrence Berkeley National Laboratory, One Cyclotron Rd., MS 53-004, Berkeley, CA 94720 USA; [2]Université Libre de Bruxelles, Indl. Chem., 50 ave. F. D. Roosevelt, CP 165/63, Bruxelles 1050 Belgium; [3]HY-Tech Research Corporation, 104 Centre Ct., Radford, VA 24141 USA

Boron carbide films are attractive materials for use as tribologcal coatings for low and high operating temperatures, especially for applications that require high hardness. We have investigated properties of boron carbide films prepared by cathodic arc using a heated B_4C cathode. The film composition is very close to that of the cathode. The effect of substrate bias on the film characteristics was studied. Hardness, elastic modulus, scratch resistance and coefficient of friction were determined for films prepared at bias voltages of: 0V, -100V and -500V. Surface morphology was also imaged with scanning electron microscopy and atomic force microscopy. It was observed that hardness and modulus increased by over 30% when a -100V bias was applied to the substrate.

4:45 PM

Mechanical Properties and Microstructural Evaluation of Chromium Containing Hard Coating on Fe-Mn-Al Alloy: *Jyh-Wei Lee*[1]; Jenq-Gong Duh[2]; [1]Tung Nan Institute of Technology, Dept. of Mechl. Eng., Taipei 222 Taiwan; [2]National Tsing Hua University, Dept. of Matls. Sci. & Eng., R405, 4th Eng. Bldg., Hsinchu 300 Taiwan

Engineering components with hard coatings usually exhibit improved service behavior and increased lifetime after appropriate surface modification. Pack chromization and r.f. magnetron sputtering techniques were employed to deposit chromium carbides and chromium nitride, respectively, on the surface of austenitic Fe-30.6Mn-6.8Al-0.9C alloy. The $(Cr,Fe)_2N_{1-x}$ and $Cr_{23}C_7$, phases were found on the chromized surface, while the internal part of chromized layer was Cr_7C_3 phase. The CrN phase was observed in the sputtered film. The phase transformation and related microstructure of chromium containing hard coatings and matrix were studied with X-ray diffractometer (XRD) and electron probe microanalyzer (EPMA). The hardness and elastic modulus of deposited coatings were evaluated by an indentation and cracking tester (ICT). Scratch tests were further conducted to investigate the adhesion of hard coatings. The conformal cracking and chipping failures were found in scratch track of chromized layer, whereas the buckling and chipping failures were observed in CrN coating. It is concluded that the chromized layer exhibits better microhardness and adhesion properties than that of sputtered film on Fe-Mn-Al alloy in the present study.

5:00 PM

Mechanical Characterization of Polymers and Glass using Instrumented Indentation: *Ethel Poiré*[1]; [1]Micro Photonics, Inc., 21 Morgan Ste. 100, Irvine, CA 92618 USA

Making small imprints and measuring optically the diagonals of indents is a well-established technique used to determine the hardness of materials and coatings. This technique can unfortunately not be used for every application. In some cases, measurement can be complicated by the tiny size of the indent or by the fact that the indent cannot be seen under the microscope because of the surface texture/appearance. This paper will present specific cases for which instrumented indentation is more advantageous as a mean to measure hardness. Instrumented indentation is based on the analysis of the load-penetration curve measured while doing an imprint. It is computer-controlled and it is not influenced by the operator's judgment of the imprint's shape. Young's modulus and fracture toughness ranking will also be presented

5:15 PM

Comparison in Characteristics of Electroless Deposited and Magnetron Sputtered Ni-P-W Coatings: *Fan-Bean Wu*[1]; Yi-Ying Tsai[2]; *Jenq-Gong Duh*[1]; [1]National Tsing Hua University, Dept. of Matls. Sci. & Eng., 429R, 4th Eng. Bldg., Hsinchu 300 Taiwan; [2]Industrial Technology Research Institute, Opto-Electr. & Sys. Labs., 908R, 51st Bldg., Chutung 310 Taiwan

Two kinds of different coating techniques, the electroless deposition and the magnetron sputtering, were employed to deposit the Ni-P-W alloy onto the stainless steel substrate. It was found that the multi-target sputtering including binary Ni-P and single W target provided a better control of the tungsten concentration in the Ni-P-W coating. Through X-ray phase identification, the sputtered Ni-P-W exhibited amorphous phase due to the co-sputtering of the tungsten, whereas metastable Ni_xP_y phases were observed in the binary Ni-P coating. The precipitation of the Ni_3P phases was retarded by the tungsten element in the coating, especially in the sputtered Ni-P-W thin film after heat treatment up to 450°C, which was higher than that for the ternary electroless Ni-P-W coating. In addition, adhesion strength and scratch failure modes for both the electroless and magnetron sputtered Ni-P-W coating were also evaluated.

5:30 PM

Cathodic Process of Electrodeposited RE-Ni-W-P-SiC Composite Coating: *Zhongcheng Guo*[1]; Xiaoyun Zhu[1]; Dacheng Zhai[1]; Keyi Ma[1]; [1]Kunming University of Science and Technology, Fac. of Matl. & Metal. Eng., Kunming 650093 China

Cathodic deposition current density of the composite coatings increases when SiC particles and rare earth (RE) were added in the bath,and it is profitable for Ni-W-P alloy to deposit in the cathod, forming Ni-W-P-SiC and RE-Ni-W-P-SiC composite coatings. On the contrary, the addition of PTFE in the bath decrease cathodic depositing current density of the coatings. The current density increases a little when the amount of RE is 7~9 g/l; however, the density increases greatly with increasing amount of RE, and it reaches peak value when the amount of RE is 11~13 g/l. But if the amount of RE is raised further, the current density decreases.

Teaching and Learning Hydrometallurgical Science and Engineering: Dissolution & Aqueous Solutions

Sponsored by: Extraction & Processing Division, Aqueous Processing Committee, Copper, Nickel, Cobalt Committee, Precious Metals Committee, Waste Treatment & Minimization Committee
Program Organizers: Kwadwo Osseo-Asare, Pennsylvania State University, Metals Science and Engineering, University Park, PA 16802-5006 USA; Saskia Duyvesteyn, University of Utah, Department of Metallurgical Engineering, Salt Lake City, UT 84112-0114 USA

Wednesday PM — Room: 601
February 20, 2002 — Location: Washington State Conv. & Trade Center

Session Chairs: Thomas W. Chapman, National Science Foundation, Div. of Cheml. & Transport Sys., 4201 Wilson Blvd., Ste. 525, Arlington, VA 22230 USA; Kenneth N. Han, SD School of Mines and Technology, Matls. & Metall. Eng., 501 E. St. Joseph St., Rapid City, SD 57701-3995 USA

2:00 PM Keynote

Dissolution of Metals in Hydrometallurgy–An Interdisciplinary Subject: *Kenneth N. Han*[1]; [1]SD School of Mines and Technology, Matls. & Metall. Eng, 501 E. St. Joseph St., Rapid City, SD 57701-3995 USA

Hydrometallurgy covers a wide spectrum of areas and its knowledge base is enlarged and enhanced by contributions from many other fields. Dissolution of metals and alloys in aqueous media will be used to illustrate how rich the field of metal extraction can be. Comprehensive understanding of the fundamentals of metal and alloy dissolution in aqueous systems requires creative application of thermodynamic prinicples, solution chemistry, ligand complexation theory, electrochemistry, transport phenomena, and heterogeneous kinetics. In addition, recent developments in instrumentation in the fields of interfacial phenomena and corrosion have tremendously advanced the field of metal extraction in aqueous systems. The close relationship between metal extraction in aqueous reactions and various physicochemical phenomena occurring in corrosion and interfacial systems will be discussed and illustrated with examples.

2:35 PM Invited
An Electrochemical Model for the Oxidation of Chalcocite by Ferric Sulfate: *David G. Dixon*[1]; *Samuel A. Bolorunduro*[1]; [1]University of British Columbia, Dept. of Metals & Matls. Eng., 309-6350 Stores Rd., Vancouver, BC V6T 1Z4 Canada

Previous kinetic studies of chalcocite oxidation have been carried out without controlling the redox potential, which is expected to fall drastically as oxidant is consumed. Considerable uncertainties arise in the interpretation and modeling of such data. In this work, oxidation of high grade chalcocite minerals in acidic ferric/ferrous sulfate solutions was investigated under controlled redox potentials. Two stages of chalcocite oxidation were observed and the rate of reaction is described by an electrochemical model in which the mixed potential is determined principally by the reversible potentials of the mineral and that of the oxidant. The first stage reaction was rapid at all temperatures and the rate is controlled by mass transfer of the oxidant to the mineral surface. The second stage reaction was characterized by the conversion of the secondary covellite to cupric ions and elemental sulfur, and the mixed potential corresponds to the reversible potential of the ferric/ferrous couple, leading to a fractional order dependence of rate on the ferric/ferrous ratio.

3:00 PM Invited
Potentiometric Measurement of pH in High Temperature Aqueous Processes: *Vladimiros G. Papangelakis*[1]; Dhehinie S. Seneviratne[1]; Xiangyang Zhou[2]; Serguei N. Lvov[2]; [1]University of Toronto, Dept. of Cheml. Eng. & Appl. Chem., 200 College St., Toronto, Ontario M5S 3E5 Canada; [2]The Pennsylvania State University, The Energy Inst. & Dept. of Energy & Geo-Environmental Eng., University Park, PA 16802 USA

The measurement of pH in pressure hydrometallurgy is gradually becoming a reality. In spite of significant advancements in the chemical modelling of high temperature aqueous systems, actual measurement of pH constitutes an important and necessary verification tool of aqueous thermodynamics. Our recent developments in this area are summarised in this communication. A novel experimental technique for measuring pH in high-temperature and concentrated process sulphate solutions is presented. An Yttria-Stabilized Zirconia sensor (YSZ) is tested on synthetic solutions simulating the hydrometallurgical processing of nickeliferous laterites by pressure acid leaching. A flow-through Ag/AgCl electrode (FTERE) is also used as an external reference electrode. Experiments were conducted using a custom-made flow-through titanium electrochemical cell specially designed for high temperature potentiometric pH measurements. Measurements were performed on simple and on progressively more complex multicomponent electrolyte solut ions containing sulphuric acid and sulphates of aluminum and magnesium. An acceptable agreement was found between the measured pH values and those predicted by theoretical calculations.

3:25 PM Invited
Systematic Modelling of Heap Leach Processes for Optimisation and Design: *Jochen Petersen*[1]; David Grant Dixon[1]; [1]University of British Columbia, Dept. of Metals & Matls. Eng., 6350 Stores Rd., Vancouver, BC V6T 1Z4 Canada

Design and operation of heap leach processes are still largely based on operator experience and rule of thumb. Although considered a low-cost, low-tech route for mineral extraction, the underlying physical, chemical and, in some cases, biological processes are actually rather complex and elude simple mathematical description. Numerous attempts have been made to model heap leaching, but the majority of models grossly simplify the true process and have remained useful only for idealised scenarios in the laboratory. There is, however, considerable interest in the minerals industry to approach design and operation of heap leach processes in a much more rigorous fashion to achieve efficient and rapid mineral extraction. To this end, a systematic process model of the heap is needed. The modelling approach presented here combines the more conventional reaction-diffusion model with models accounting for heat conservation, chemical speciation in solution, bacterial growth and propagation, 3D axis-symmetrical bulk adve ction-diffusion flow, gas flow, etc. The model versatility and applicability are demonstrated with a number of scenarios investigated in recent laboratory and field studies. It becomes clear that both, a flexible modelling tool and a systematic laboratory/pilot investigation, are necessary to fully appreciate the complexity of any particular heap leach scenario. Once such a comprehensive model is in place, however, optimisation of existing operations or optimal design of new heaps are relatively straightforward.

3:50 PM Break

4:00 PM Invited
Magnetic Activated Carbon: An Old Product with a New Future: *Saskia Duyvesteyn*[1]; Gustavo A. Munoz[1]; Jan D. Miller[1]; [1]University of Utah, Metlgcl. Eng., 135 S. 1460 E., Rm. 412, Salt Lake City, UT 84112-0114 USA

While the concept of activated carbon that is magnetic is not new, a new magnetic activated carbon (MAC) product has been developed at the University of Utah. The MAC is produced by mixing a fine particulate carbon source with a magnetic precursor and subjecting the mixture to a series of chemical and heat treatments. The fine particle size results in rapid adsorption kinetics, and the magnetic properties allow for recovery from solutions or slurries by means of magnetic separation. The characteristics of MAC for gold adsorption from alkaline cyanide solutions, such as capacity, selectivity, and elution will be discussed in terms of particle size, surface area, and, of particular importance, in terms of surface functional groups. The influence of surface modification on uptake of heavy metal ions, such as Cu, Cd and Zn, will be discussed as well.

4:20 PM Invited
A Tutorial on Synthesis and Use of Adsorbents for Hydrometallurgical Separations: *Lawrence L. Tavlarides*[1]; [1]Syracuse University, Cheml. Eng., 334 Hinds Hall, Syracuse, NY 13244 USA

The presentation will describe methods to synthesize adsorbents for targeted metal ion separations for the hydrometallurgical industry. Functional group selection and various methods of sorbent synthesis such as covalent attachment and sol-gel techniques will be described. Characterization of these materials will be illustrated with specific examples. The utility of several sorbents will be shown for examples such as noble metal separation and acid mine drainage cleanup.

4:45 PM Invited
NSF Programs Related to Hydrometallurgy: *Thomas W. Chapman*[1]; [1]National Science Foundation, Div. of Cheml. & Transport Sys., 4201 Wilson Blvd., Ste. 525, Arlington, VA 22230 USA

The mission of the National Science Foundation (NSF) is to advance the nation's welfare by promoting scientific progress. Specific goals involve the development of people, ideas, and tools for science and engineering. This presentation will provide an overview of NSF programs that are relevant to the advancement of hydrometallurgy. These programs include support of not only academic research but also educational development and collaboration between universities and industry. Examples will be given of specific research projects funded by NSF and related to hydrometallurgical processes.

5:10 PM Invited
A Short History of Hydrometallurgy: *Fathi Habashi*[1]; [1]Laval University, Dept. of Mining, Metlgcl., & Matls. Eng., Quebec City, Quebec G1K 7P4 Canada

Thousands of years ago people had learned how to build furnaces and use fire to melt rocks and produce metals but the use of water and aqueous solutions for ore processing came much later, mainly at the time of the alchemists when acids and alkalies became known and used. Modern hydrometallurgy, however, can be traced back to the end of the nineteenth century when two major operations were discovered: the cyanidation process for gold and silver extraction and the Bayer Process for bauxite treatment. Later, in the 1940's, a breakthrough came during the Manhattan Project in USA in connection with uranium extraction. Since then, it has been advancing progressively and even replacing some pyrometallurgical processes. Canadian contribution is significant particularly in the recovery of uranium, nickel, cobalt, and zinc.

Many changes have been made to the boiler during the last decades. The new boiler design and optimization were carried out by using physical water and air-dust modeling as well as computational fluid dynamics. The modeling work agree well with experiences in practice. The latest developments have increased the operating hours per year and the effectiveness of the waste heat boiler.

Third International Sulfide Smelting Symposium - "Sulfide Smelting '02": Zinc, Lead and PGM's

Sponsored by: Extraction & Processing Division, Pyrometallurgy Committee, Copper, Nickel, Cobalt Committee, Lead, Zinc, and Tin Committee, Non-Ferrous Metals Committee
Program Organizers: Robert L. Stephens, TeckCominco Metals, Ltd., Trail, British Columbia V1R 4L8 Canada; Hong Yong Sohn, University of Utah, Department of Metallurgical Engineering, Salt Lake City, UT 84112 USA

Wednesday PM	Room: 607
February 20, 2002	Location: Washington State Conv. & Trade Center

Session Chairs: Andreas H. Siegmund, RSR Technologies Incorporated, 2777 Stemmons Hwy., Ste. 1800, Dallas, TX 75207 USA; Markus A. Reuter, Delft University of Technology, Appl. Earth Scis., 2628 Rx Delft, Mijnbouwstraat 120, Delft 2628 RX The Netherlands

2:00 PM
The Behaviour of Iron as Impurity in Zinc Roasting: *Satu Jyrkönen*[1]; Pekka A. Taskinen[1]; Maija-Leena Metsärinta[1]; Aija Rytioja[2]; Jens Nyberg[2]; [1]Outokumpu, Outokumpu Rsrch. Oy, PO Box 60, Pori FIN-28101 Finland; [2]Outokumpu Zinc Oy, PO Box 26, Kokkola FIN-67101 Finland

In Kokkola Zinc smelter as well as in most other roasting plants it is a trend towards using concentrates with increasing impurity content nowadays. This also often means that the size distribution of the concentrates gets finer. Iron is present with highest percentage as a single impurity. The behavior of iron in zinc roasting was studied in laboratory experiments. Commercial zinc concentrates with low and high (1.5-16 wt-%) iron content as pyrite or in the lattice of sphalerite were partially roasted to establish the reaction mechanisms of iron in roasting. Microscopical studies were carried out on the calcine, and the findings were presented in numerous photographs of the polished cross sections. SEM/EDS was used for analyzing the phases present in the samples. A calcination mechanism of zinc concentrates with high iron content was suggested.

2:25 PM
Agglomeration in Zinc Fluidized Bed Roasters: *J. Pierre Constantineau*[1]; John R. Grace[1]; Greg G. Richards[2]; C. J. Lim[1]; [1]University of British Columbia, Chem. & Bio. Eng., 2216 Main Mall, Vancouver, BC V6T 1Z4 Canada; [2]Cominco Research, Trail, BC V1R 4S4 Canada

The use of fluidized beds for the roasting of zinc sulphide concentrates has been of major benefit in the electrolytic production of zinc. The operation consists of reacting zinc sulphide with air or oxygen-enriched air to produce zinc oxide (calcine), subsequently acid-leached, and sulphur dioxide, directed to a sulphuric acid plant. The fluidized bed roasting process aims at maximizing the sulphide conversion, minimizing sulphate and zinc ferrite production, while maintaining excellent productivity. Stable operation of fluidized bed zinc roasters requires an adequate particle size distribution to minimize the risk of defluidization and to help maintain carryover within manageable levels. However, the understanding of the roasting process is limited and changes in operating conditions mainly rely on intuition, experience, and trial and error. A research program has been initiated at UBC to study the phenomena that influence the particle size distribution of the fluidized bed. This paper will present the approach, describe the apparatus that has been constructed and provide some preliminary results on the agglomeration phenomena occurring during fluidized bed roasting of industrial zinc concentrates.

2:50 PM
Improvements of Zinc Roaster Waste Heat Boiler: *Juha Järvi*[1]; Jussi Vaarno[1]; Jens Nyberg[2]; Heikki Siirilä[2]; [1]Outokumpu Research Oy, PO Box 60, Pori FIN-28101 Finland; [2]Outokumpu Zinc Oy, PO Box 26, Kokkola FIN-67101 Finland

Outokumpu Zinc Oy has two separate roasting lines with fluidized bed furnaces and waste heat boilers for calcine collection and heat recovery. During the last 30 years the zinc production in Kokkola plant has continuously increased and at the same time raw-materials have changed. Therefore the waste heat boiler has been under continuous research and development. The waste heat boiler has a significant role in the process and therefore the reliability and the efficiency of the device is important for the effectiveness of the entire process.

3:15 PM
Technology for Processing of Lead-Bearing Materials from Copper Metallurgy at KGHM Polska Miedz S.A.: *Ryszard Prajsnar*[1]; Zbigniew Smieszek[1]; Jozef Czernecki[1]; Seweryn Plucilski[2]; Marian Warmuz[2]; Leszek Garycki[2]; [1]Institute of Non-Ferrous Metals, ul. Sowinskiego 5, 44-100 Gliwice Poland; [2]KGHM Polska Miedz S.A., HM Glogow, ul. Zukowicka 1, 67-231 Zukowice Poland

During copper producting in shaft and flash smelting processes at KGHM Polska Miedz S.A., lead-bearing material of sulfide, sulfate, and oxide character is generated such as slime from shaft furnace gas handling systems, converter dusts, and dusts from an electric furnace for copper removal from flash smelting slag. These materials are polymetallic concentrates of Pb, Zn, and Cu, with As, Cl, and Cd as impurities. Shaft furnace slime, containing about 50% PbS and 15% bituminous substances, is the main lead-bearing material. At the Glogow copper mill, a new plant was commisioned in June, 2001 to process 80,000 tonnes per year of lead bearing materials to produce 26,000 tonnes per year of crude lead. The plant consists of a feed conditioning system, three rotary rocking furnaces with a capacity of 16 tonnes of lead feed fired with natural gas and oxygen-enriched air containing up to 45 vol% O_2, and a gas handling system. The gas handling system includes a post-combustion chamber, a gas cooling chamber with Cl neutralization, gas mixing chamber, bag filter, and dry limestone scrubbing system for SO_2 removal. The lead-bearing feed is smelted with 5wt% sodium carbonate and 13wt% iron scrap at a temperature of 950-1050°C for 3 hours. The smelting process consists of 4 stages; feed drying, firing of gaseous hydrocarbons and solid coal from the feed, lead reduction from slag, and separation of molten products. The flow rates of natural gas and oxygen to the burners are controlled to ensure combustion of the bituminous material in the furnace. The process produces crude lead bullion containing (wt%) 0.1 to 0.5% Cu, 0.02 to 0.5% As, 0.05 to 0.07% Bi, 0.1 to 0.5% Sb, 0.1 to 0.6%Sn. The process also produces a micture of sodium silicate slag, Fe-Zn-Pb-Cu-S matte, and Fe-As speiss containing (wt%) 5 to 10% Pb, 2 to 6% Cu, 10 to 15% Zn, 1 to 3% As, 10 to 15% S, 0.5 to 3.0% Cl, 2 to 4% K, 4 to 7% Na, 20 to 30% Fe, and 5 to 10% SiO_2. The dust is made up of PbO, ZnO, $PbSO_4$ and $PbCl_2$, KCl, and NaCl with a chemical composition (wt%) of 35 to 50% Pb, 5 to 15% Zn, 3 to 6% As, 4 to 8% Cl, 2 to 5% K, and 2 to 5% Na. The construction of the new lead production plant at the Glogow copper mill will process both current lead-bearing materials as well as lead-bearing material that have been stockpiled over the last 15 years to give a significant improvement in protection of the natural environment.

3:40 PM Break

3:55 PM
ConRoast: DC Arc Smelting of Dead-Roasted Sulphide Concentrates: *Rodney T. Jones*[1]; [1]Mintek, Pyrometall. Div., PB X3015, Randburg 2125 S. Africa

Mintek has developed and piloted a novel process for the treatment of nickel-copper and PGM (platinum group metal) sulphide concentrates. The ConRoast process is based on the removal of sulphur by roasting, followed by smelting of the dead-roasted concentrate in a DC arc furnace, using an iron-based alloy as a collector for nickel, copper, cobalt, and PGMs. The environmental benefits with respect to sulphur emissions are considerable, in that essentially all of the sulphur is removed from the enclosed roasting equipment in a continuous stream of SO2 of an appropriate strength for feeding to a sulphuric acid plant. This process allows great flexibility with respect to the selection of ore types, and does not impose limits on the minimum quantities of contained base metals or sulphur, and can tolerate very high contents of chromite in the concentrate. The furnace alloy is water-atomized prior to leaching. Iron may be rejected from the alloy hydrometallurgically, by precipitation as hematite for example. The ConRoast process achieves very high metal recoveries, and produces high-purity metals, and a clean high-grade PGM concentrate.

4:20 PM
Online Prediction of Actual Melt Chemistry in an Ausmelt Converter using a Thermodynamic-System Identification Hybrid Modeling Technique: *Jacques J. Eksteen*[1]; G. A. Georgalli[1]; Markus A. Reuter[2]; [1]University of Stellenbosch, Dept. of Cheml. Eng., PB X1, Matieland, Western Cape 7602 S. Africa; [2]Delft University of

Technology, Dept. of Raw Matls. Tech., Mijnbouwstraat 120, Delft 2628 RX The Netherlands

Lance based copper-nickel matte converters have become an established technology in the field of base metal sulphide smelting and converting. An AusmeltÒ converter is currently being constructed at Anlgo Platinum in South Africa to convert a nickel-copper rich matte containing platinum group metals (PGM's). The accurate prediction of the matte chemistry is required to control the composition at the endpoint which influences segregation of PGM's during the subsequent slow cooling and magnetic separation processes. A hybrid modelling approach is introduced in this paper that incorporates both the effect of thermochemistry and system dynamics. It will be shown how the model relates to fundamental conservation laws, while still providing enough flexibility to adapt to changing operating conditions. It will also show off-line modelling can be incorporated into a robust on-line model. Based on the data from many pilot plant trials, the model prediction performance is shown to be within the accuracy requirement set by industry and therefore constitutes a reliable basis for model based control.

4:45 PM

Platinum from a Chrome Furnace–It's a Matter of Design: *Bruce Nourse*[1]; J. Malan[1]; R. Moolman[1]; H. Joubert[1]; [1]Pyromet Technologies (Pty.), Ltd., PO Box 61582, Marshalltown 2107 S. Africa

The depressed market for Ferrochrome worldwide has forced most producers in this industry to scale down production. Inevitably, many furnaces have been mothballed for prolonged periods, awaiting an upturn in the Ferrochrome market. In contrast, the Platinum industry is experiencing relative stability combined with good prices and they have been looking for cash cows to take advantage of these market conditions. It is, therefore, rather convenient that Platinum and Ferrochrome producers are virtually neighbours in the Bushveld complex of South Africa, since there is an abundance of spare furnace capacity around (albeit for Ferrochrome). Against this backdrop, Pyromet Technologies (Pty) Ltd, who are currently designing a slag cleaning furnace for Anglo Platinum, was requested to perform pilot scale testwork on a 200kW furnace, in order to establish the suitability to process platinum concentrate and converter slag in a furnace designed for Ferrochrome. This paper provides an overview of the configuration, test conditions, operation and results achieved during the testwork. It also discusses the critical issues, such as refractory consumption, copper cooling and electrical parameters that need to be addressed when converting a Ferrochrome Smelter into a Sulphide Smelter.

Third International Sulfide Smelting Symposium - "Sulfide Smelting '02": Sulfide Smelting Fundamentals II

Sponsored by: Extraction & Processing Division, Pyrometallurgy Committee, Copper, Nickel, Cobalt Committee, Lead, Zinc, and Tin Committee, Non-Ferrous Metals Committee

Program Organizers: Robert L. Stephens, TeckCominco Metals, Ltd., Trail, British Columbia V1R 4L8 Canada; Hong Yong Sohn, University of Utah, Department of Metallurgical Engineering, Salt Lake City, UT 84112 USA

Wednesday PM	Room: 609
February 20, 2002	Location: Washington State Conv. & Trade Center

Session Chairs: Fathi Habashi, Laval University, Dept. of Mining, Metlgcl. & Matls. Eng., Quebec City, Quebec G1K 7P4 Canada; Adrian C. Deneys, Praxair Inc., 777 Old Saw Mill River Rd., Bldg. 765, Tarrytown, NY 10591-6714 USA

2:00 PM

Thermophysicochemical Database for Batch or Continuous Processes in Nickel Smelting and Converting: *F. Kongoli*[1]; I. McBow[1]; S. Llubani[1]; [1]Flogen Technologies, Inc., 5757 Decelles Ave., Bureau 511, Montreal, QC H3S 2C3 Canada

A computerized thermophysicochemical database is being developed for various processes involved in nickel smelting and converting. This database includes optimized models for slag, matte, liquid and solid alloys in the multicomponent system(s) as applied to nickel smelting and converting processes, batch or continuing ones. This database can be used to quantify the multicomponent and multiphase slag/matte/alloy/gas phase equilibria, liquidus and solidus surface, tie-lines, solubility and/or losses of nickel and other components in the slag, distribution coefficient, components activities, heat and mass balance, etc. The database also includes optimized models for the viscosity of the slags associated with any of the above processes. Both databases are coupled and this constitute a very effective method to quantify the effect of each component on several parameters of the smelting and converting processes and to diffuse the considerable confusion that exist in the literature. Several application examples have been given to demonstrate the usefulness of this database for quantitative prediction of the thermophysicochemical properties of the phases involved in actual or developing processes, even in the areas where experiments are difficult or impossible. The considerable cost reduction that results from the use of this database as compared to other methods in the improvement of existing technologies or in the development of new ones is discussed along with continuing new developments of this database.

2:25 PM

Quantification of the Liquidus Surface of Some Iron Oxide Slags of Industrial Interest at Constant CO2/CO Ratio: *Florian Kongoli*[1]; Akira Yazawa[2]; [1]Flogen Technologies, Inc., Metall., 5757 Decelles Ave., Ste. 511, Montreal, QC H3S 2C3 Canada; [2]Tohoku University, 16-32, Niizaka, Aoba-ku, Sendai 981-0934 Japan

Liquidus surface of multicomponent slags is an important parameter in various smelting and converting processes. It helps not only to optimize the slag chemistry of current processes and their fluxing strategies, but also to determine the availability of new slags for more advanced technologies. In a series of our previous publications, the liquidus surface of some multicomponent iron oxide slags has been quantified at several constant oxygen potentials and the effect of the latter, ignored until that moment, was quantified along with the effect of some minor components. In this work, the liquidus surface of some iron oxide slags is quantified at constant CO2/CO ratios. This is a new convenient way for the quantitative description of the slag liquidus surface as well as of the effect of several fluxes, especially in those processes, such as slag solidification, where the oxygen potential changes continuously. This type of diagram also describes more dynamically the effect of oxygen potential, clarifies the relation between CO2/CO ratio and oxygen potential in terms of the liquidus surface (not widely understood by metallurgist today) and reduces the gap between laboratory work and industrial experience.

2:50 PM Invited

Phase Relations and Activities in the Cu-Fe-S-As and Cu-Fe-S-Sb Systems at 1473K: Dexter G. Mendoza[1]; Hector M. Henao[1]; Mitsuhisa Hino[1]; Kimio Itagaki[1]; [1]Tohoku University, Inst. of Multidisciplinary Rsrch. for Adv. Matls., 2-1-1 Katahira, Aoba-ku, Sendai, Miyagi 980-8577 Japan

Knowledge of thermodynamic properties of minor elements in the copper matte is of practical importance for understanding their behaviors in the copper smelting processes. In the present study, phase relations and activities of arsenic and antimony as minor elements in each miscibility gap in the Cu-Fe-S-As and Cu-Fe-S-Sb systems were determined at 1473K by using a quenching method and a double Knudsen-cell mass spectrometer method, respectively. The distribution ratios of arsenic and antimony between the matte and metal phases were around 0.1, that means both elements distribute preferentially into the metal phase. The molar ratio of NFe/NCu in the miscibility gap had no serious effect on the distribution ratio. The activity coefficients of arsenic and antimony in the matte phase were found to be about one order of magnitude larger than those in the metal phase. By using the obtained data, elimination of arsenic and antimony in the copper phase by means of slagging was discussed and the fractional distribution of these elements among the gas, slag, matte and metal phases was thermodynamically evaluated.

3:15 PM Invited

Phase Equilibrium between Ni-S Melt and Slags under Controlled Partial Pressures: *Hector M. Henao*[1]; Mitsuhisa Hino[1]; Kimio Itagaki[1]; [1]Tohoku University, Inst. for Multidisciplinary Rsrch. for Adv. Matls., Katahira 2-1-1, Aoba-Ku, Sendai, Miyagi 980-8577 Japan

To provide thermodynamic data for converting nickel matte to liquid nickel at high temperature, an experimental study was conducted on the phase equilibrium between the Ni-S alloy and the FeO_X-SiO_2, FeO_X-CaO or CaO-Al_2O_3 base slag in a MgO crucible at 1773 K under controlled PSO_2 of 0.1 atm and PO_2 in a range between $5x10^{-7}$ and 10^{-5} atm by using CO-CO_2-SO_2 gas mixtures. The distribution ratio of nickel between the slag and alloy phases at a given PO_2 was found to be minimum for the CaO-Al_2O_3-MgO slag with NCaO/NAl_2O_3 molar ratio of 1.7. The solubility of nickel in this slag at PO_2 of $6x10^{-6}$ atm (just before the precipitation of solid NiO) was 5 mass %. These results suggest the availability of CaO-Al_2O_3 base slag in converting the Ni-S melt to nickel.

3:40 PM Break

3:55 PM Moved to Monday AM
Kinetics of Sulfide Smelting in Mitsubishi Process: *Zenjiro Asaki*

4:20 PM
Predicting Phase Equilibria in Oxide and Sulphide Systems: *John A. Gisby*[1]; Alan Dinsdale[1]; Ian Barton-Jones[2]; Alan Gibbon[3]; Pekka A. Taskinen[4]; Jeff R. Taylor[5]; [1]National Physical Laboratory, NPL Matls. Ctr., Queens Rd., Teddington, Middlesex TW11 0LW UK; [2]Rio Tinto, PO Box 50, Castlemead, Lower Castle St., Bristol BS99 7YR UK; [3]Mineral Industry Research Organisation, 75 Peppard Rd., Sonning Common, Berkshire RG4 9RN UK; [4]Outokumpu Research Oy, PO Box 60, Pori FIN-28101 Finland; [5]Johnson Matthey Technology Centre, Sonning Common, Reading, Berkshire RG4 9NH UK

Phase equilibria for multi-component systems can be calculated reliably from critically assessed thermodynamic data for smaller sub-systems using software packages like MTDATA, written at the National Physical Laboratory (NPL). Models and data developed in an ongoing Mineral Industry Research Organisation (MIRO) project make such calculations possible for the complex systems encountered during sulphide smelting, involving interactions between matte, slag, metal and gas phases. Predictive calculations can be made which are directly relevant to industrial processes, covering composition and temperature ranges beyond the scope of hard-copy phase diagram compilations, allowing the feasibility of more economic and environmentally sound routes to be explored, better choices of materials to be made and pilot plant studies to be directed more efficiently. Current applications include the selection of suitable fluxing practices in copper and nickel smelting, analysing the operation of the Kennecott copper smelter, optimising the recovery of precious metals and investigating refractory wear.

4:45 PM
Minor Element Distribution between Copper Matte and Reverb Furnace Slag: *Natasa Mitevska*[1]; Zivan D. Zivkovic[2]; [1]Copper Institute, Zeleni Bulevar 35, Bor 19120 Yugoslavia; [2]Belgrade University, Tech. Fac., Bor 19210 Yugoslavia

The control of minor element behaviour during pyrometallurgical processing of copper concentrate is very important for anode copper production as well as influencing the production economics and minimizing environmental impact. The transfer of minor elements from the matte to the slag can be considered as either impurity elimination or loss of valuable components into the slag. On the basis of chemical analyses of samples taken during stable operation of the No.2 reverb furnace in the Copper Smelter and Refinery, RTB BOR (Yugoslavia), the distribution coefficients for Ag, As, Au, Bi, Co, Cu, Ni, Pb, Sb, Se, Te, and Zn between copper matte and slag are determined. The influence of the matte grade on the minor element distribution coefficients between copper matte and slag is also analyzed.

5:10 PM Cancelled
Simulation of Combustion in Copper Flash Smelter: *Xin-feng Li*

Notes