# TMS2003

**132nd Annual International Meeting & Exhibition**

**The Minerals, Metals & Materials Society welcomes you to the TECHNICAL PROGRAM for the 132nd TMS Annual Meeting & Exhibition, to be held March 2–6, 2003, in San Diego, California.**

*This document comprises*

## TUESDAY'S TECHNICAL PROGRAM

*Including fully text-searchable paper titles, abstracts, and author names with affiliations*

***For your convenience, we have also included details on***

- Meeting Activities and Registration
- Conference Proceedings
- Our Exhibition
- TMS Membership
- Additional On-line Resources that You May Utilize

***All designed to help you prepare for— and optimally benefit from— one of the world's premier metals and materials events.***

**See you in San Diego!**

http://www.tms.org/AnnualMeeting.html

# AN INTERNATIONAL EVENT IN SCIENCE AND ENGINEERING

*During the week of March 2–6, the 2003 TMS Annual Meeting & Exhibition will host approximately 4,000 science and engineering professionals, representing more than 70 different countries. They are convening at the San Diego Convention Center and the San Diego Marriott Hotel & Marina to attend a field-spanning array of metals and materials symposia containing more than 200 sessions and 1,900 individual technical presentations.*

*This year's meeting will feature programming by*

- TMS Electronic, Magnetic & Photonic Materials Division
- TMS Extraction & Processing Division
- TMS Light Metals Division
- TMS Materials Processing & Manufacturing Division
- TMS Structural Materials Division
- TMS Education Committee
- TMS Young Leaders Committee
- ASM International's Materials Science Critical Technologies Sector
- Aluminum Association
- International Magnesium Association

*In addition to the technical programming featured on the following pages, attendees will have the opportunity to*

- **Tour** the Exhibition of Approximately 200 Companies Displaying New Products and Services
- **Attend** Special Lectures and Tutorials
- **Participate** in Short Courses on Sulfide Smelting, Magnesium Metallurgy, Heat Treating Aluminum Alloys, Process Heating, Pumping Systems, and Computational Materials
- **Enjoy** Special Luncheons, Dinners, and Social Functions, including events honoring Ronald Armstrong, Michael Messhi, and Akira Yazawa
- **Network** Extensively
- **Experience** the Charm and Amenities of Family-Friendly San Diego

*Extensive details about these and all conference-related activities can be found on the 2003 TMS Annual Meeting Web Site.*

# WANT TO BE PART OF THE ACTION?

*Registration is easy.*

Just complete and mail or fax the Annual Meeting Registration Form that appears in this document. Or, visit the meeting web site to register immediately (and securely) on-line.

To register in advance, your submission must reach TMS not later than **February 3, 2003.** After this date, it will be necessary to register at the meeting site.

The **San Diego Marriott Hotel & Marina** is the TMS headquarters hotel. Special conference rates have been contracted with this hotel and others in the area surrounding the **San Diego Convention Center.** To receive special rates, use the TMS 2003 Housing Reservation Form that appears in this document and that can be found on the meeting web site.

**Special Opportunity for TMS Nonmember Registrants:** All nonmember registrants automatically receive a one-year introductory associate membership in TMS for 2003. Membership benefits include a subscription to *JOM* (print and on-line versions) and significant discounts on TMS products and services.

*More on the benefits of membership appears on the TMS Membership Web Pages.*

# INTERESTED IN BUSINESS OPPORTUNITIES?

The 2003 TMS Annual Meeting & Exhibition presents businesses, universities, institutions, agencies, consultants, and others with myriad opportunities to partner in effective marketing communication. Such opportunities to reach thousands of meeting attendees include:

- Placing a **Booth** in the Exhibition
- Placing an **Ad** in the Official Conference Publication and At-Meeting Program: *JOM*
- Sponsoring High-Profile **Attendee Services,** such as the CyberCenter, Coffee Breaks, Signage, and Prize Drawings.
- Hosting a **Hospitality Suite**

*More information on these opportunities is available on the 2003 TMS Annual Meeting Sponsorship Web Pages.*

# CONFERENCE PROCEEDINGS: THE RECORDS OF EVENTS

*The technical program of each TMS Annual Meeting yields numerous conference proceedings that document many presentations delivered in session rooms. Such publications can be ordered both before and after the meeting via the meeting registration form and/or the TMS Document Center.*

*The following symposium proceedings will be available in tandem with the meeting.*

- ***Electron Microscopy: Its Role in Materials Science***: The Mike Meshii Symposium on Electron Microscopy
- ***EPD Congress 2003*** (Documenting the Symposia Global Development of Copper and Gold Deposits; Mercury Management; Recycling, General; Residue Handling in Metals Processing; Sensors and Control in Materials Processing; Waste from Metal Plating Industries)
- ***Friction Stir Welding and Processing II***
- ***High Temperature Alloys: Processing for Properties***
- ***Hot Deformation of Aluminum Alloys 2003***
- ***Light Metals 2003*** (Documenting the Symposia Alumina and Bauxite; Aluminum Reduction Technology; Carbon Technology; Cast Shop Technology; Reactive Metals; Recycling, Aluminum)
- ***Magnesium Technology 2003***
- ***Materials Lifetime Science and Engineering***
- ***Metallurgical and Materials Processing Principles and Technologies: The Yazawa International Symposium***
  - Volume 1: *Fundamentals and New Technologies*
  - Volume 2: *High Temperature Metal Production*
  - Volume 3: *Aqueous and Electrochemical Process*
- ***MPMD Fourth Global Innovations Symposium: Energy Efficient Manufacturing Processes***
- ***Surface Engineering in Materials Science II***

*The following proceedings volumes will be released shortly after the meeting.*

- ***Aluminum Reduction: Potroom Operations***
- ***Aluminum 2003*** (Documenting the Symposia Automotive Alloys 2003; Universities Servicing Education, Research, and Technology Internationally for the Aluminum and Light Metals Industries; Increasing Energy Efficiency in Aluminum)
- ***Gamma Titanium Aluminides 2003***

*The following symposia will be documented in upcoming TMS periodicals.*

- Advances in MEMS and Optical Packaging (*Journal of Electronic Materials*)
- Applications and Processing of Powder Metallurgy Refractory Metals and Alloys (*JOM*)
- Computational Methods in Materials Education (*JOM*)
- Dynamic Deformation: Constitutive Modeling, Grain Size, and Other Effects: Symposium in Honor of Prof. Ronald W. Armstrong (*Metallurgical and Materials Transactions A*)
- Lead-Free Solders and Processing Issues Relevant to Microelectronics Packaging (*Journal of Electronic Materials*)
- Materials and Processes for Submicron Technologies III (*Journal of Electronic Materials*)
- Phase Stability, Phase Transformations, and Reactive Phase Formation in Electronic Materials (*Journal of Electronic Materials*)
- Terence E. Mitchell Symposium on the Magic of Materials: Structures and Properties (*Metallurgical and Materials Transactions A*)

*Detailed information about these publications, and many others, can be found in the TMS Document Center.*

# ADDITIONAL RESOURCES

*On-line answers to any of your 2003 TMS Annual Meeting & Exhibition questions can be found at*

- **2003 TMS Annual Meeting & Exhibition Web Site:** Get up-to-the-minute meeting details and complete registration materials at http://www.tms.org/AnnualMeeting.html
- **TMS Personal Conference Scheduler:** Review the most-up-to-date version of the technical program, examine the calendar of events, and create your own personalized itinerary by visiting http://pcs.tms.org
- **TMS Document Center:** Review the complete tables of contents for conference proceedings and order publications by visiting http://doc.tms.org
- **TMS Membership:** Learn more about the benefits of membership by touring http://www.tms.org/Society/membership.html
- **TMS Business-to-Business Partnering:** Learn how TMS can help your organization maximize its impact by viewing http://www.tms.org/Meetings/Annual-03/Annual03-exhibit.html

*If you want to contact a person, more details are available at*

TMS Meetings Department
The Minerals, Metals & Materials Society
184 Thorn Hill Road, Warrendale, PA 15086 USA
Telephone: (724) 776-9000, ext. 243
Fax: (724) 776-3770
E-mail: mtgserv@tms.org

# TMS2003

## ADVANCE REGISTRATION FORM

**Advance Registration Deadline: February 3, 2003**

**Payment must accompany form.** AM03-PDF
Forms received past this date will be processed at the on-site fee.

**WEB** http://www.tms.org
Web registration requires credit card payment.

**FAX** USA: 724-776-3770
Fax registration requires credit card payment.

**MAIL** **Return with payment to:** TMS, Meeting Services
184 Thorn Hill Road
Warrendale, PA 15086

**1.** ☐ Dr. ☐ Prof. ☐ Mr. ☐ Mrs. ☐ Ms. ____________ Member of: ☐ TMS ☐ ISS ☐ SME ☐ SPE Member Number:____________

Last Name First Name Middle Initial

Employer/Affiliation:____________ Title:____________

Address: ☐ Business ☐ Home ____________

City:____________ State/Province:____________ Zip/Postal Code:____________ Country:____________

Telephone:____________ Fax:____________ E-Mail:____________

Guest/Spouse Name:____________ *Guests do not receive admission to technical sessions.*

### 2. Registration Fees:

| | Advance Fees until February 3, 2003 | | On-Site Fees after February 3, 2003 | |
|---|---|---|---|---|
| ☐ Member | $400 | M | $500 | ML |
| ☐ Non-member Author* | $455 | NMA | $555 | NMAL |
| ☐ Non-member * | $525 | NM | $625 | NML |
| ☐ Student Member ## | $0 | STU | $0 | STUL |
| ☐ Student Non-member ## * | $25 | STUN | $25 | STUNL |
| ☐ TMS Senior Member | $225 | RM | $225 | RML |
| ☐ Exhibit Booth Personnel | $0 | E | $0 | EL |
| ☐ Exhibit Only | $35 | EO | $35 | EOL |

Registration TOTAL $ ________

** Includes TMS membership for 2003*
*## Students must attach a copy of their school's student identification card.*

### 3. Social Function Tickets:

| Day | Event | Fee | Quantity | Total |
|---|---|---|---|---|
| Monday 3/3/03 | Michael Meshii Honorary Dinner | $60 | ____ | $_____ MD |
| | Akira Yazawa Honorary Dinner | $60 | ____ | $_____ YD |
| | Ronald Armstrong Honorary Dinner | $60 | ____ | $_____ RD |
| Tuesday 3/4/03 | 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 3/5/03 | Light Metals Division Luncheon | $30 | ____ | $_____ LM |
| | Tables of 8 | $240 | ____ | $_____ LM8 |
| | Table Sign to Read ____________ | | | |
| | Structural Materials Division Luncheon | $30 | ____ | $_____ SM |
| | Tables of 8 | $240 | ____ | $_____ SM8 |
| | Table Sign to Read ____________ | | | |
| | Gamma Titanium Aluminides Dinner | $60 | ____ | $_____ GTD |

Social Function TOTAL $ ________

### 4. Tutorial Luncheon Tickets:

| Monday 3/3/03 | Fee | Quantity | Total |
|---|---|---|---|
| *The Young Leader Tutorial Lecture is free.* | | | |
| *You may purchase the optional box lunch for* | $25 | ____ | $_____ EM |

### 5. Publication Orders: *All orders that are not indicated for shipment on this form must be picked-up at the meeting.*

| Order Number | Title | Shipping Weight | Quantity | SubTotal Weight | Member Price | Non-member Price | Sub-Total Price |
|---|---|---|---|---|---|---|---|
| 03-5352 | Electron Microscopy (Meshii) | 3 | ______ | ______ | $96 | $137 | $ ________ |
| 03-5344 | Metallurgical & Materials Processing (Yazawa)—Three-volume Set | 11 | ______ | ______ | $337 | $538 | $ ________ |
| 03-5468 | Vol. 1: Fundamentals & New Technologies *(only)* | 4 | ______ | ______ | $154 | $220 | $ ________ |
| 03-5476 | Vol. 2: High-Temp. Metal Production *(only)* | 4 | ______ | ______ | $154 | $220 | $ ________ |
| 03-5484 | Vol. 3: Aqueous & Electrochemical Process *(only)* | 3 | ______ | ______ | $112 | $159 | $ ________ |
| 03-5328 | EPD Congress 2003 | 3 | ______ | ______ | $87 | $123 | $ ________ |
| 03-531X-G | Light Metals 2003 *(book and CD set)* | 7 | ______ | ______ | $158 | $226 | $ ________ |
| 03-5360 | Friction Stir Welding and Processing II | 3 | ______ | ______ | $110 | $157 | $ ________ |
| 03-5336-G | Magnesium Technology 2003 *(book and CD set)* | 3 | ______ | ______ | $113 | $161 | $ ________ |
| 03-5395 | High Temperature Alloys | 2 | ______ | ______ | $75 | $107 | $ ________ |
| 03-5387 | Hot Deformation of Aluminum Alloys 2003 | 4 | ______ | ______ | $123 | $175 | $ ________ |
| 03-5441 | Materials Lifetime Science & Engineering | 2 | ______ | ______ | $91 | $130 | $ ________ |
| 03-5379 | Surface Engineering in Materials Science II | 2 | ______ | ______ | $124 | $177 | $ ________ |
| 03-5522 | Energy Efficient Manufacturing Processes (4th MPMD Global Symp.) | 2 | ______ | ______ | $65 | $92 | $ ________ |

SubTotal $ ________

**WEIGHT AND ZONE CHART**

| Weight | USA | Canada | Mexico | Western Europe | Eastern Europe | Australia, New Zealand | Central, South America | Pac. Rim, Asia | Middle East, India, Africa |
|---|---|---|---|---|---|---|---|---|---|
| 1 | $2.50 | $4.00 | $4.50 | $4.00 | $5.00 | $4.50 | $5.00 | $5.00 | $6.50 |
| 2 | $3.00 | $5.00 | $9.00 | $8.00 | $10.00 | $9.00 | $10.00 | $10.00 | $13.00 |
| 3 | $3.50 | $6.00 | $13.50 | $12.00 | $15.00 | $13.50 | $15.00 | $15.00 | $19.50 |
| 4 | $4.00 | $7.00 | $18.00 | $16.00 | $20.00 | $18.00 | $20.00 | $20.00 | $26.00 |
| 5 | $4.50 | $8.00 | $22.50 | $20.00 | $25.00 | $22.50 | $25.00 | $25.00 | $32.50 |
| 6 | $5.00 | $9.00 | $27.00 | $24.00 | $30.00 | $27.00 | $30.00 | $30.00 | $39.00 |
| 7 | $5.50 | $10.00 | $31.50 | $28.00 | $35.00 | $31.50 | $35.00 | $35.00 | $45.50 |
| 8 | $6.00 | $11.00 | $36.00 | $32.00 | $40.00 | $36.00 | $40.00 | $40.00 | $52.00 |
| 9 | $6.50 | $12.00 | $40.50 | $36.00 | $45.00 | $40.50 | $45.00 | $45.00 | $58.50 |
| 10 | $7.00 | $13.00 | $45.00 | $40.00 | $50.00 | $45.00 | $50.00 | $50.00 | $65.00 |
| 11 | $7.50 | $14.00 | $49.50 | $44.00 | $55.00 | $49.50 | $55.00 | $55.00 | $71.50 |
| 12 | $8.00 | $15.00 | $54.00 | $48.00 | $60.00 | $54.00 | $60.00 | $60.00 | $78.00 |

*If books are to be shipped, please complete the following.*

Total Weight ______ Calculate shipping fees from the chart (at left) $ ________

$5 handling fee per order shipped. $ ________

**NOTE:** *If your order exceeds 12 pounds, add the amount that is over from the chart (at the left) to reach the total weight of your order. [Example: 16 lbs. (delivered in U.S.A.) would be 12 lbs. ($8.00) + 4 lbs ($4.00) = 16 lbs. ($12.00)]*

Publications TOTAL $ ________

### 6. Continuing Education Short Courses: *Saturday & Sunday, March 1-2, 2003*

| | Advance Fees until February 3, 2003 Member | Non-member | On-Site Fees after February 3, 2003 Member | Non-member |
|---|---|---|---|---|
| ☐ 1. Sulfide Smelting: Principles, Technologies, and Environmental Considerations (Sat./Sun.) | $645 | $735 | $695 | $785 |
| ☐ 2. Magnesium Metallurgy—Processing and Industrial Applications (Sat./Sun.) | $645 | $735 | $695 | $785 |
| ☐ 3. Heat Treatment of Wrought and Cast Aluminum Alloys (Sat./Sun.) | $645 | $735 | $695 | $785 |
| ☐ 4. Process Heating Workshop—Jt. TMS/DOE (Sat.) | $475 | $560 | $525 | $610 |
| ☐ 5. Pumping Systems Assessment Workshop - Jt. TMS/DOE (Sun.) | $475 | $560 | $525 | $610 |
| ☐ 6. Computational Materials Design (Sun.) | $475 | $560 | $525 | $610 |

Short Course TOTAL $ ______ $ _______

### 7. 2003 Membership Dues: *For current TMS members only*

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

### 8. 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: ____________

### 9. TOTAL FEES PAID ....$____________

**Refund policy:** Written requests must be mailed to TMS, post-marked no later than February 3, 2003. A $50 processing fee will be charged for all cancellations. No refunds will be processed after February 3, 2003.

# TMS2003

**132nd Annual International Meeting & Exhibition**
**March 2-6, 2003 • San Diego, California, USA**

## HOUSING RESERVATION FORM

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)

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!

**Reservations must be received at Travel Planners by: Monday, February 3, 2003**

Arrival Date ______________________ Departure Date ______________________

Last Name ______________________ First Name ______________________ MI __________

Company ______________________

Street ______________________ Address ______________________

City ______________ State/County ______________ Zip/Postal Code ______________ Country ______________

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 ______________________

**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

**HEADQUARTERS**

1 **San Diego Marriott Hotel & Marina**
$212/s/d • $232/bayview

2 **Clarion Hotel**
$125/single • $125/double

3 **Westgate Hotel**
$160/single • $160/double

4 **The Horton Grand Hotel**
$169/single • $169/double

5 **Hyatt Regency San Diego**
$239/single • $239/double

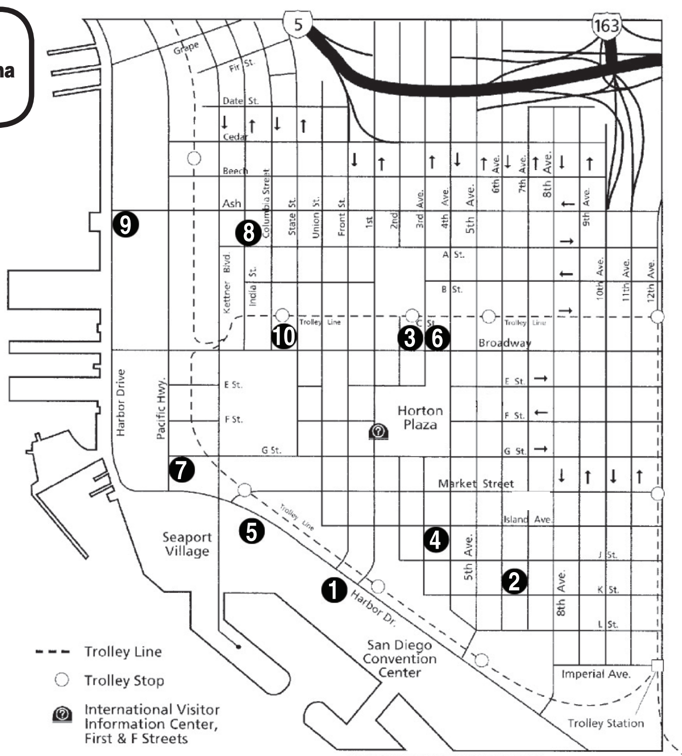
6 **U.S. Grant Hotel**
$179/single • $179/double

7 **Embassy Suites Hotel**
$190/single • $210/double

8 **Best Western Bayside Inn**
$124/single • $124/double

9 **Holiday Inn – on The Bay**
$165/single • $165/double

10 **Wyndham Emerald Plaza Hotel**
$179/single • $179/double




***TMS has contracted a block of rooms at the headquarters hotel, San Diego Marriott Hotel & Marina, 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 132nd TMS Annual Meeting & Exhibition by making your reservation at one of the listed hotels prior to the advance housing deadline. Thank you.***

**Confirmations:** Confirmations 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. (If canceling or changing a room at the Hyatt after February 20, 2003, you must call the Hyatt 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.***

**Deposit Payment:** ☐ Check ☐ American Express ☐ MasterCard ☐ VISA ☐ Discover ☐ Diners

Account Number ______________________ Expiration Date ______________

Card Holder Name ______________________ Authorized Signature ______________________

## Actinide Materials: Processing, Characterization, and Behavior: Plutonium

*Sponsored by:* Light Metals Division, Structural Materials Division, ASM International: Materials Science Critical Technology Sector, SMD-Nuclear Materials Committee-(Jt. ASM-MSCTS), LMD-Reactive Metals Committee
*Program Organizers:* Sean M. McDeavitt, Argonne National Laboratory, Chemical Technology Division Materials Development Section, Argonne, IL 60439-4837 USA; Michael F. Stevens, Los Alamos National Laboratory, Los Alamos, NM 87545 USA

Tuesday AM — Room: 4
March 4, 2003 — Location: San Diego Convention Center

*Session Chair:* Sean M. McDeavitt, Argonne National Laboratory, Cheml. Tech. Div. Matls. Dvlp. Sect., Argonne, IL 60439-4837 USA

**8:30 AM Keynote**
**An Overview of Plutonium: Metal, Ceramics, and Chemistry**: *Siegfried S. Hecker*[1]; [1]Los Alamos National Laboratory, MST-DO, MS G754, Los Alamos, NM 87545 USA

Plutonium is the most complex element. It sits near the middle of the actinide series and appears to occupy a unique position with no analogues. In the solid state, the 5f electrons in plutonium are caught in an abrupt transition between being bonding and being localized, giving rise to very unusual propertiesñespecially its instability with temperature, pressure, and chemistry. It is highly reactive in moist air and strongly reducing in solution, forming multiple compounds and complexes in the environment and during chemical processing. In molecular bonding, the proximity of the 7s, 6d, and 5f electrons in valence orbitals generates a strong competition among these configurations while the 5f electrons extend sufficiently far to favor highly directional bonding. Plutonium transmutes by radioactive decay, damaging its crystalline lattice and leaving behind helium and other transmutation products in solids and causing radiolytic effects in solution or in organic materials.

**9:15 AM**
**Thermal Expansion and Gr¸neisen Ratio of Invar-Like δ-Phase Pu-Ga Alloys**: *Andrew C. Lawson*[1]; Joyce A. Roberts[2]; Barbara Martinez[3]; [1]Los Alamos National Laboratory, Matls. Sci. & Tech. Div., MS H-805, Los Alamos, NM 87545 USA; [2]Los Alamos National Laboratory, Los Alamos Neutron Sci. Ctr., MS H845, Los Alamos, NM 87545 USA; [3]Los Alamos National Laboratory, Nucl. Matls. Tech. Div., MS E574, Los Alamos, NM 87545 USA

Recently we showed that the thermal expansion behavior of Pu-Ga follows the Weiss two-state model for the invar effect developed for Fe-Ni alloys. In δ-phase Pu, the thermal expansion behavior is determined by a competition between the normal lattice expansion with the expansion associated with the thermal occupation of two localized states, a lower-energy higher volume state $\delta_1$, and a higher energy lower volume state $\delta_2$. Higher temperature favors the occupation of the lower volume state. Using model parameters appropriate for Pu-Ga, we discuss the consequences of the invar model for these alloys: atomic volume, thermal expansion and Gr¸neisen constant versus temperature and Ga concentration. The competition between two thermal expansion mechanisms leads to anomalous behaviors for these quantities.

**9:35 AM**
**Thermodynamic Assessment of the Stability Properties of Pu-Based Alloys: Application of the Calphad Methodology**: *Patrice E.A. Turchi*[1]; Patrick G. Allen[1]; Shihuai Zhou[2]; Zi-Kui Liu[2]; Larry Kaufman[3]; [1]Lawrence Livermore National Laboratory, Dept. of Chem. & Matls. Sci., PO Box 808, Livermore, CA 94551 USA; [2]The Pennsylvania State University, Dept. of Matls. Sci. & Eng., University Park, PA 16803 USA; [3]Massachusetts Institute of Technology, Dept. of Matls. Sci. & Eng., Cambridge, MA 02139 USA

The CALPHAD approach has been applied to the study of the equilibrium thermodynamic properties of Pu-X alloys (X=Al,Fe,Ga,Ni). Predictions are made on the low temperature phase diagrams of Pu-Ga and Pu-Al for which controversy has been noted in the past. The validity of the assessed thermodynamics is discussed by comparing predicted heats of transformation with measured values from DSC analysis. An overall picture for the stability properties of Pu-Ga and Pu-Al that reconciles the results of past studies carried out on these alloys is proposed. Additional assessment will be presented for the Pu-Ni system. Finally preliminary results are presented on TTT diagrams for some of the reactions occurring in Pu-Ga alloys, and suggestions are made for further studies. This work was performed under the auspices of the US Department of Energy by the University of California Lawrence Livermore National Laboratory under Contract W-7405-ENG-48.

**9:55 AM**
**Mechanical Behavior of Delta-Phase Plutonium-Gallium Alloys**: *George C. Kaschner*[1]; Michael G. Stout[1]; Siegfried S. Hecker[2]; [1]Los Alamos National Laboratory, Matls. Sci. & Tech. Div., MST-8, MS G755, Los Alamos, NM 87545 USA; [2]Los Alamos National Laboratory, Matls. Sci. & Tech. Div., MST-DO, MS G754, Los Alamos, NM 87545 USA

In this report, we present a constitutive model that predicts the yield strength and ultimate tensile strength (UTS) of delta-stabilized plutonium-gallium alloys (Pu-Ga). The model accounts for the effects of temperature, strain rate, grain size, and gallium (Ga) concentration. The coefficients in the model are based on ambient-pressure quasi-static data that were published in the open literature. Our model has been validated against approximately 50 different experiments for both yield and ultimate strength. The predicted yield strengths agreed with the experimental data to within a ±1 standard deviation of 15%. The gallium concentration has the greatest affect on the yield strength. There was a 50% increase in yield strength ranging from Pu-1 at % Ga to Pu-6 at % Ga. The grain size also produced a measurable strengthening effect, typical of face-centered-cubic (fcc) metals. The yield strength for a material with 10 µm grain size was 15% greater than for 50 µm grain size. Finally, we found that there were no observable yield strength effects from different amounts of either iron and nickel impurities or carbon concentrations.

**10:15 AM Break**

**10:35 AM**
**Electron Backscatter Diffraction of Plutonium-Gallium Alloys**: *Carl J. Boehlert*[1]; Thomas G. Zocco[2]; Roland K. Schulze[2]; Jeremy N. Mitchell[2]; Ramiro A. Pereyra[2]; [1]Alfred University, Sch. of Ceram. Eng. & Matls. Sci., CEMS/McMahon Hall, 2 Pine St., Alfred, NY 14802 USA; [2]Los Alamos National Laboratory, Nucl. Matls. Tech., MS G721, Los Alamos, NM 87545 USA

An experimental technique has been developed to characterize reactive metals, including plutonium and cerium, using electron backscatter diffraction (EBSD). Microstructural characterization of plutonium and its alloys by EBSD had been previously elusive primarily because of the extreme toxicity and rapid surface oxidation rate associated with plutonium metal. The experimental techniques, which included ion-sputtering the metal surface using a scanning auger microprobe (SAM) followed by vacuum transfer of the sample from the SAM to the scanning electron microscope (SEM), used to obtain electron backscatter diffraction Kikuchi patterns (EBSPs) and orientation maps for plutonium-gallium alloys are described and preliminary microstructural observations based on the analysis are discussed. Combining the SEM and EBSD observations, the phase transformation behavior between the d and e structures was explained. This demonstrated sample preparation and characterization technique is expected to be a powerful means to further understand phase transformation behavior, orientation relationships, and texture in the complicated plutonium alloy systems.

**10:55 AM**
**Influence of Fe on Elevated Temperature Phase Transformations in Pu-0.6 Wt.% Ga**: *Daniel S. Schwartz*[1]; Thomas G. Zocco[1]; Ramiro A. Pereyra[1]; Michael Ramos[1]; [1]Los Alamos National Laboratory, NMT-16, PO Box 1663, MS G721, Los Alamos, NM 87545 USA

Low concentrations of Fe are thought to have a significant effect upon phase transformations and homogenization kinetics in lean Pu-Ga alloys above 400C. In order to study this effect in detail, differential scanning calorimetry (DSC) and optical microscopy were used to examine phase transformations in Pu-0.6 wt.% Ga containing ~300 wppm Fe. A series of specimens cut from a casting of Pu-0.6 wt.% Ga + 300 wppm Fe were given 24 hour anneals at temperatures ranging from 450C to 510C. The specimens were subsequently scanned in the DSC from RT to 580C. The α-β and δ-ε solid state transformations and the $Pu_6Fe$ melt transition were examined in detail. Material annealed above ~480C showed significant qualitative and quantitative differences compared to material annealed at the lower temperatures. The observed differences and their ramifications will be discussed in detail.

**11:15 AM**
**Atomistic Determination of the Transport Properties of Liquid Plutonium-Gallium Alloys**: *Frank J. Cherne*[1]; Michael I. Baskes[1]; [1]Los Alamos National Laboratory, MST-8, Struct. & Prop. Rel., PO Box 1663, MS G755, Los Alamos, NM 87545 USA

The transport properties of liquid plutonium-gallium alloys are calculated using equilibrium and non-equilibrium techniques. The potentials chosen for our study are based on the modified embedded atom method. These potentials have been shown to be representative of Pu/Ga system. The calculated transport coefficients, diffusivity and viscosity, are evaluated across the entire composition range (0-100% gallium). The calculated viscosity is found to be much greater than the available experimental data. The range of temperatures evaluated are between 950 K and 1700 K.

**11:35 AM**
**Atomistic Modeling of the Phase Stability in the Pu-Ga System**: *Krishna Muralidharan*[1]; M. I. Baskes[1]; Marius Stan[1]; S. G. Srinivasan[1]; [1]Los Alamos National Laboratory, MST-8, Los Alamos, NM 87545 USA

The plutonium (Pu)-gallium (Ga) system has a complex equilibrium phase diagram consisting of about twenty phases. There is still considerable disagreement in the literature regarding the existence of a eutectoid point in the Pu-Ga phase diagram. In this work, we calculate the Pu rich (XGa < 0.25) part of the phase diagram using a combination of molecular dynamics (MD) and thermochemical calculations, with the recently developed MEAM potential used to represent the interatomic interactions. This potential was shown to be quite reliable in predicting the stable phases of the pure Pu and the Ga systems. The phase diagram is constructed by calculating the free energies of the various phases as a function of temperature and composition. The resultant phase diagram will be compared and contrasted to existing experimental data.



## Alumina and Bauxite: Red Mud Operations

*Sponsored by:* Light Metals Division, LMD-Aluminum Committee
*Program Organizers:* David Kirkpatrick, Kaiser Aluminum & Chemical Group, Gramercy, LA 70052-3370 USA; Steve Rosenberg, Worsley Alumina Pty, Ltd., Process Chemistry Group, Collie, West Australia 6225 Australia; Paul Crepeau, General Motors Corporation, MC/486-710-251, Pontiac, MI 48340-2920 USA

Tuesday AM — Room: 3
March 4, 2003 — Location: San Diego Convention Center

*Session Chairs:* David Kirkpatrick, Kaiser Aluminum & Chemical Group, Gramercy, LA 70052-3370 USA; Steve Rosenberg, Worsley Alumina Pty Ltd., Process Chem. Grp., Collie, W. Australia 6225 Australia

**8:30 AM**
**Influence of Bayer Liquor Composition on the Measurement of Slurry Velocity Using an Electrochemical Flowmeter**: *AndrÈ Leclerc*[1]; Alexandre Perron[1]; Guy Simard[1]; Michel J. Gagnon[1]; Guy Peloquin[2]; [1]UniversitÈ du QuÈbec ‡ Chicoutimi, Dept. Scis., 555 Blvd. de lÍUniversitÈ, Chicoutimi, QuÈbec G7H 2B1 Canada; [2]Alcan International Ltd., Jonquiere, Quebec G7S 4K8 Canada

A knowledge of the flow velocities in the feed well of sequential gravity settlers of the Bayer process is essential for their optimal design and operation. The velocities range from 0 to 50 cm/s and the characteristics of the Bayer liquor vary between settlers. An intrusive electrochemical flowmeter described previously may be used to measure slurry velocities in the 5 to 50 cm/s range with a precision of 10% by monitoring an electrical current. This current depends not only on the fluid velocity but also on the characteristics of the Bayer liquor. The principal physical parameter is the temperature since the electrochemical reaction rates and physical properties are temperature dependant. The chemical parameters are the concentrations of the major solutes that partake in the electrochemical reaction or that affect the activies of the reagents. To use this flowmeter, calibration curves relating the current as a function of the temperature and the concentrations of sodium hydroxide, carbonate and aluminate must be available. Typical concentration curves are presented and discussed.

**8:55 AM**
**A Fractal Model for the Aggregate Size Distributions Generated During Red Mud Flocculation**: *Michel J. Gagnon*[1]; Andre Leclerc[1]; Guy Simard[1]; Guy Peloquin[2]; [1]Universite du Quebec at Chicoutimi, Dept. Scis., 555 Blvd. Universite, Chicoutimi, Quebec G7H 2B1 Canada; [2]Alcan International Ltd., 1955 Blvd. Melon, Jonquiere, Quebec G7S 4K8 Canada

In the Bayer process, flocculation is produced in the gravity settlers to enhance the settling of the fine particles of red mud. Depending upon many physical and chemical parameters, the aggregates generated demonstrate specific density-size distributions. In this study, a fractal model of the flocculation process is introduced. Based on reliable experimental data and on physical calculation, the model presented helps to envisage the initial formation of the aggregates, and to interpret the subsequent interactions between the aggregates in terms of a global flocculation process. A good agreement is obtained between the model and the experimental data.

**9:20 AM**
**Effect of Organics on the Separating Efficiency of Flocculates in Red Mud Sedimentation**: *Zhijian Lu*[1]; [1]Henan Filiale of China Aluminium Company, Tech. Dept., Shangjie Dist., Zhengzhou, Henan 450041 China

Adding flocculates is an important method to facilitate the separating of red mud slurry in alumina refinery, while the existence of organics will disturb their separating efficiency. The effect of seven organics (benaenedicarboxylic sodium, phenol, oxalic sodium, formic sodium,acetic sodium, yellow and black humic acid) on overfall clarity, underflow L/S and sedimentation rate in red mud separating procedure by using three anionic flocculates such as A-600, HPAM, PAS-1 and one nonionic flocculate (PAM) had been researched respectively in this paper. It is illustrated that the existence of organics can significantly decrease the separating efficiency of flocculates. The optimum concentration of flocculates in slurry increase with the rising of organics and the negative effect of organic canít be eliminated when its content higher than a certain value which is different for every organic. However, A-600 has best separating effect for all experiments while the effect of nonionic flocculate PAM is indistinctive.

**9:45 AM**
**Security Filtration Operation in CVG-Bauxilum**: Ricardo Alfredo Galarraga[1]; [1]CVG-Bauxilum, Lado Rojo II, Zona Industrial Matanzas, Puerto Ordaz, BolÌvar 8015 Venezuela

The segurity filtraciÛn area ( 38 area ), is essential in the Bayer process of alumina production. In CVG-Bauxilum this area to consist in 16 Kelly filters of 36 m3 of capacity and 372 m2 of filtration area by filter. Around of 19 years of plant operation has been maked changes structural and operational for improve the performance. The changes of mesh of the filtres frames, the increase the flow across of the frames, the time the operation of the filters, the frequency of washed acid and caustic, the cloths life and the relation of TCA are some changes done in the industrial area. This work involve the more important changes done until today for improve the area for to serve the levels of production demanding.

**10:10 AM Break**

**10:20 AM**
**Settling Properties and Utilization of Red Mud Produced in Bayer Process with an Excessive Addition Lime**: *Zhao Hengqin*[1]; Feng Ansheng[1]; Li Jie[2]; Liu Yexiang[2]; [1]Zhengzhou Institute of Mulitipurpose Utilization of Mineral Resources, No 328 Longhai W. Rd., Zhengzhou, Henan 450006 China; [2]Central South University, Sch. of Metallurgl. Sci. & Eng., Changsha, Hunan 410083 China

Good settling property of red mud is one of what contribute to smooth production of alumina. In this paper, the study has been performed on the settling properties of red mud produced in Bayer Process with an excessive addition lime. The results indicated that the settling property of red mud produced in the Bayer Process with an excessive addition lime are slightly poorer than that in conventional Bayer Process, but the former red mud with smaller ratio of L/S, and can meet the requirements of production process of alumina. As for red mud produced in the above improved Bayer Process,its utilization has also been studied, and the research results showed that the red mud can be used as raw material of silicate cement.

**10:45 AM**
**Conversion of Conventional Wet Disposal of Red Mud into Thickened Tailing Disposal (TTD) at Nalco Alumina Refinery, Damanjodi**: *S. K. Banerjee*[1]; [1]National Aluminium Company, Ltd., Dir. (Proj. & Techls.), Bhubaneswar 751013 India

National Aluminum Company (NALCO) is a leading company in India to successfully implement the environmental friendly Thickened Tailing Disposal (TTD) System for disposal of red mud produced from itís Alumina Refinery. Earlier, the red mud was disposed of in a pond using conventional wet disposal method with a solid concentration of 25-30%. The TTD system, introduced recently under the expansion program, is operated with high rate thickeners and positive displacement pumps to dispose of the red mud at a solid concentraion of 55-65% on the existing pond. The introduction of this new system has resulted in substantial savings in capital cost in construction of a new pond apart from saving in energy cost for recycling of water from the red mud pond. The detailed engineering for the system was done by Engineers India Tld. and the system was supplied by M/S Envirotech, Netherlands at an approximate cost of USD 15 million.

**11:10 AM**

**Experience with Thickened Disposal of Red Mud**: *Pitabas Das*[1]; D. Roy[1]; [1]National Aluminum Company Ltd., R&D, Orissa State 00085 India

Due to the obvious environmental impact emanating from disposal of Red Mud, it has always posed to be a sticky problem for Alumina Plants. Ever tightening environmental regulations have been forcing Alumina producers worldwide to continuously look for better and safer methods of disposing the red mud generated by them. As most pollution controllers consider traditional method of disposal in wet form, a potential threat to environment, the trend now is to switch over to a dry disposal mode, or otherwise termed as the Thickened Tailings Disposal (TTD) system. National Aluminium Company (NALCO) in India has recently commissioned a TTD System. This paper elaborates the advantages and disadvantages experienced with the system so far.

**11:35 AM**

**Problems of Red Mud DisposalñIs Romelt an Answer?**: *S. K. Misra*[1]; J. S. Saluja[2]; [1]National Aluminum Company, Ltd., Rsrch., Dvpt. & Eng., P/1, Nayapali, NALCO Bhawan, Bhubaneswar 751013 India; [2]Romelt Sail India, Ltd., A-47, Friends Colony (East), New Delhi-65 110065 India

Bauxite Residue (Red Mud) is the major waste from Alumina Refineries which are contaminated with alkali and pose serious environmental hazards. NALCOís alumina refinery having an annual capacity of 1.575 Million tones per annum disposes red mud in specially designed ponds around its refinery. The Bauxite having 25-30% iron content in the form of oxides offers tremendous scope for waste utilization and mitigation of environmental hazards. Several methods for extraction of iron from low grade ores and wastes are now available. Moscow Institute of Steel and Alloys (MISA) after intensive research for iron making have developed the Romelt Technology which accepts the microfine iron oxides without any pretreatment. NALCO after getting promising results from the laboratory testing of its red mud are now taking steps for preparation of a feasibility report for a Romelt Plant which will substantially eliminate the problem of waste disposal apart from maintaining the ecological balance.

## Aluminum Reduction Technology: Environmental - HF and PFC

*Sponsored by:* Light Metals Division, LMD-Aluminum Committee
*Program Organizers:* Jay Bruggeman, Alcoa Inc., Alcoa Center, PA 15069 USA; Martin Segatz, VAW Aluminum Technology, Bonn D-53117 Germany; Paul Crepeau, General Motors Corporation, MC/ 486-710-251, Pontiac, MI 48340-2920 USA

Tuesday AM — Room: 6B
March 4, 2003 — Location: San Diego Convention Center

*Session Chair:* Jerry Marks, J. Marks and Associates, Kansas City, MO 64064 USA

**8:30 AM**

**The Effect of Pot Operation and Work Practices on Gaseous and Particulate Fluoride Evolution**: *G. P. Tarcy*[1]; [1]Alcoa Inc., Hall Process Improvement, Alcoa Techl. Ctr., 100 Alcoa Dr., Alcoa Ctr., PA 15069-0001 USA

Alcoa has measured fluoride evolution (amount of fluoride in the duct off a single pot) intermittently since 1980. In 1982 and 1983, continuous real time measurements were made of gaseous HF and total fluoride on a series of single pots ranging from 20 kA to 275 kA. The information was cataloged as a function of pot operations including alumina feeding, anode effect, crust integrity, anode change, bath chemistry changes and metal tapping. The studies showed that the single most important factor to both gaseous HF evolution and particulate evolution was the integrity of the crust. As the crust integrity deteriorated into open holes, the amount of HF evolution increased up to a limiting rate while the particulate evolution increased without any indication of a limit being reached. The studies also showed that under ideal operations (good crust integrity and no upsets), approximately 16% of the fluoride evolved from the pot was due to feeding of alumina and the evolution associated with this was due to water on the material, not fluoride or crust breaking. Anode effect and the method by which they are terminated also impact the fluoride evolution, as does anode change and the method by which the anode is covered. Metal tapping has a very short-lived high evolution rate associated with this practice.

**8:55 AM**

**The Impact of Open Holes on Vapor-Phase Fluoride Evolution from Pots**: *Michael L. Slaugenhaupt*[1]; Jay N. Bruggeman[1]; Gary P. Tarcy[1]; Neal R. Dando[2]; [1]Alcoa Inc., Hall Process Improvement, Alcoa Techl. Ctr., 100 Alcoa Dr., Alcoa Ctr., PA 15069-0001 USA; [2]Alcoa Inc., Alcoa Techl. Ctr., 100 Technical Dr., Alcoa Ctr., PA 15069-0001 USA

Pot operating and tending practices are the primary determinants of fluoride evolution. Fluctuations in fluoride evolution have direct consequences on pot gas scrubber loads, which can impact scrubber maintenance and capture efficiency. Variability in fluoride evolution can also have dramatic implications on bath chemistry control. Both of these factors motivate continuing efforts to quantify the affect of pot operating practices on fluoride evolution. Gaseous fluoride evolution measurements were made at several smelters and quantitatively demonstrate a strong correlation between the amount of vapor-phase fluoride evolved from individual pots and the total area of open holes in the crust. Data from pots of different operating types suggests that it is possible to normalize the data to allow predictions for other pot sizes and geometries. In many cases, the additional fluorides lost due to holes in the crust comprise the largest fraction of the total gaseous evolution.

**9:20 AM**

**In-Plant PFC Monitoring: Technology Options and Performance Concerns**: *Neal R. Dando*[1]; [1]Alcoa Inc., 100 Technical Dr., Alcoa Ctr., PA 15069-0001 USA

Commercial aluminum production is the largest emission source of the perfluorocarbon gases (PFCs) carbon tetrafluoride(CF4) and hexafluoroethane (C2F6). Given the high global warming potentials of these two gases, concerted efforts exist to monitor and reduce future emissions of PFCs from aluminum smelters. Several commercially available technologies exist for enabling capable off-line and on-line in-plant monitoring of PFC emissions. The local conditions in aluminum smelters (duct gas composition, magnetic fields, etc.) present a hostile environment for most instrumentation, which can compromise the accuracy and stability of the analysis method. This paper will detail a comparative evaluation of the advantages and disadvantages of different technologies for off-line and/or on-line in-plant PFC monitoring. Practical concerns regarding sample handling and method implementation will be discussed with respect to each monitoring approach.

**9:45 AM**

**Tunable Laser Diode Technology for Continuous HF Monitoring in Potrooms**: *Carl Kamme*[1]; [1]Opsis, Inc., 1165 Linda Vista Dr., San Marcos, CA 92069 USA

A tunable diode laser (TDL) provides an excellent tool for potroom open path measurements of gaseous HF. The TDL provides quick and exact concentration data for HF from one or several potrooms. Monitoring is provided for reporting purposes, and also process control. Particular events in the smelting process can be measured and evaluated in terms of gaseous emissions, which allows for savings and process improvements. Technology now supports automatic system alignment of the optical laser beam, which compensates for any changes in building structure caused by thermal stress or crane movements.

**10:10 AM Break**

**10:20 AM**

**A Streamlined Portable Mid-IR TDL Based System for On-Site Monitoring of PFCís from Potroom Exhaust Ducts**: *H. A. Gamble*[1]; D. R. Karecki[1]; G. I. Mackay[1]; H. I. Schiff[1]; [1]Unisearch Associates, Inc., 96 Bradwick Dr., Concord, Ont. L4K 1K8 Canada

Maintaining comprehensive and up to date records of the quantities of perfluorocarbons (PFCís) emitted from potroom exhaust ducts is an issue of outstanding concern to primary producers of aluminium worldwide. Unisearch has previously demonstrated the utility of mid-IR tunable diode laser based instrumentation for performing detailed, accurate, on site measurements of PFCís (CF4 and C2F6). The Unisearch TAMS-150 has been used for on-site measurements of PFCís at primary aluminium smelters across Canada, over a period of time spanning more than ten years. Unisearch now presents a more streamlined version of the instrument, the EMS-150, capable of performing the same experiment and of producing similar or better quality results. The instrument has been developed at Unisearch in response to ongoing industry needs, and is available either as a commercial instrument or on a contract measurement basis.

**10:45 AM**

**Protocol for Measurement of Tetrafluoromethane and Hexafluoroethane from Primary Aluminum Production**: *Jerry Marks*[2]; *Ravi Kantamaneni*[1]; *Diana Pape*[1]; *Sally Rand*[3]; [1]ICF Consulting, 1850 K St. NW, Ste. 1000, Washington, DC 20006 USA; [2]J. Marks and Associates, Kansas City, MO 64064 USA; [3]US Environmental Protection Agency, 1200 Pennsylvania Ave. NW, 6202J, Washington, DC 20460 USA

Two perfluorinated compounds (PFCs), tetrafluoromethane (CF4) and hexafluoroethane (C2F6), are produced periodically during primary aluminum production by the Hall-Heroult process. The atmospheric concentration of these two compounds is currently about 81 parts per trillion by volume (pptv) CF4 and 3 pptv C2F6 based on projections of previously reported measurements. While the annual amount of CF4 and C2F6 released to the atmosphere is small in comparison to other greenhouse gases, the environmental impact of each yearís emissions will persist for generations due to their long atmospheric lifetimes, estimated at 50,000 and 10,000 years, respectively. The measurement of PFCs is required to assist with developing the most accurate greenhouse gas emissions inventories. These inventories can be used to support company benchmarking and process improvement activities, to facilitate reporting under the United Nations Framework Convention on Climate Change, and to assist with the implementation of emissions trading mechanisms. This paper describes a measurement protocol to assist with developing accurate PFC inventories based on the Intergovernmental Panel on Climate Change (IPCC) Tier 3b method. The protocol has been produced with an aim to foster consistency in smelter-specific sampling programs. The procedure described here provides a method for making accurate measurements of CF4 and C2F6 emissions and relating those measurements to anode effect process data. A methodology is presented for summarizing the collected data and calculating IPCC Tier 3b emission factors, which provide for the most accurate calculation of long term PFC emissions from aluminum production. The protocol provides the necessary guidance to allow individual facilities to develop detailed plans for sampling and analysis based on plant specific technology, anode effect data, and chosen measurement instrumentation.

**11:10 AM**

**Measuring Reporting and Verifying GHG Emissions from Aluminum Smelting Operations**: *Kenneth Joseph Martchek*[1]; [1]Alcoa Inc., ABSS, 201 Isabella St., ACC-5B08, Pittsburgh, PA 15212 USA

Emissions of gases such as CO2 which retain heat in our atmosphere from bauxite refining, anode production, aluminum smelting and indirectly from electricity to power aluminum electrolysis has been estimated worldwide at 350-400 million metric tons of carbon dioxide equivalents per year. In particular, persistent greenhouse gases, CF4 and C2F6, are emitted during ìanode effectsî and the worldwide industry has responded by reducing these perfluorocarbon emissions by 46% since 1990. Nevertheless, accurately measuring, reporting and verifying all significant greenhouse gas emissions from aluminum operations is becoming increasingly important because of emerging schemes related to taxation, allowances, emissions trading, regulatory and reporting requirements. This paper highlights recent efforts in developing a robust and coherent greenhouse gas emissions inventory for alumina refining, carbon consumption and aluminum electrolysis in todayís regime of developing corporate, regional, state and international protocols. This paper will highlight practical ìlessons learnedî from a pilot third-party verification of greenhouse gas emissions measurements and reporting at an alumina refinery, an aluminum smelter and a dedicated coal-based electricity generator. In particular, this paper will discuss issues such as data quality, records retention and integration of emissions measurement into a locationís ISO 14,001 compliant Environmental Management System.

**11:35 AM**

**PFC Emissions Measurements from Aluminium Pechiney Smelters**: *CÈline Martin*[1]; Elisabeth Couzinie[1]; [1]Aluminium Pechiney, LRF, BP 114, Saint-Jean-de-Maurienne, Cedex 73303 France

Emissions of CF4 and C2F6 were measured with a photoacoustic gas spectrometer for three different AP smelters: 300 kA PFPB pots, 93 kA PFPB pots and 105 kA SWPB pots. Gases were directly extracted from the exhaust ducts between the pots and the dry Gas Treatment Centre to obtain continuous measurements. Fugitive emissions were considered to be insignificant for the modern PFPB pots whereas samples of gases were collected from the roof exhaust gas of the SWPB smelter. In this case, a collection efficiency was determined for PFC during anode effects. For each smelter, emissions measured were related to the anode effect overvoltage in order to be confronted to the Aluminium Pechiney equation. For the 300 kA PFPB pots, anode effect overvoltage and anode effect duration were also recorded in order to compare the Pechiney Overvoltage method and the Slope method. Relevance and accuracy of both methods is discussed.

## Carbon Technology - I

*Sponsored by:* Light Metals Division, LMD-Aluminum Committee
*Program Organizers:* Amir A. Mirchi, Alcan Inc., Arvida Research and Development Centre, Jonquiere, QC G7S 4K8 Canada; Don T. Walton, Alcoa Inc., Wenatchee Works, Malaga, WA 98828-9784 USA; Paul Crepeau, General Motors Corporation, MC/486-710-251, Pontiac, MI 48340-2920 USA

Tuesday AM — Room: 6D
March 4, 2003 — Location: San Diego Convention Center

*Session Chair:* Frank Cannova, BP, Petroleum Coke Marketing, Long Beach, CA 90802 USA

**8:30 AM**

**Formulation/Structure and Properties of Carbon Anodes from Coal-Tar Pitch/Petroleum Pitch Blends**: Marta PÈrez[1]; *Marcos Granda*[1]; Ricardo SantamarÌa[1]; Roberto GarcÌa[1]; Rosa MenÈndez[1]; [1]Instituto Nacional del CarbÛn, CSIC, Chem. of Matls., C/Francisco Pintado Fe, 26, Oviedo, Asturias 33011 Spain

During the last decade much effort has been devoted to overcoming environmental problems derived from the use of traditional coal-tar pitch in Sˆderberg pot rooms. To this end, coal-tar pitch/petroleum pitch blends have been developed with the aim of obtaining a low PAH content. This would result in lower PAH emissions. The use of these blends in the preparation of carbon anodes requires a new paste formulation. This is because blends are usually more fluid than coal-tar pitches. For this reason, modifications in the granulometric coke fractions and binder percentage must be made. This paper reports on the formulation of pastes from coal-tar pitch/petroleum pitch blends and on the structure and properties of the resultant carbon anodes.

**8:55 AM**

**Precise Measurement of Density of Coal Tar Oil and Liquid Binder Pitch**: *Kwangeui Yoon*[1]; Myoung Won Lee[1]; Dong Joon Lee[1]; Se In Yang[1]; [1]DC Chemical Company, Ltd., R&D Ctr., 587-102, Hakik-Dong, Nam-Gu, Incheon 402-772 Korea

The density of liquid pitch is an essential factor for the mass of the pitch amount at elevated temperature. To operate anode plant at optimum condition, accurate weight measurement of liquid binder pitch is very important. However there has been no adequate system to measure the precise density at high temperature and not much data in public. We modified the conventional density measurement system of buoyant force to a system with high temperature measuring cell which could measure the liquid density at high temperature with very high accuracy. Using this system, we measured high temperature densities of coal tar fractions. Also densities of various coal tar binder pitches were measured in the temperature range of 190-210°C where liquid pitch is practically handling. We tried to correlate these high temperature density with their typical properties.

**9:20 AM**

**Worldwide Pitch Quality for Anodes**: *Raymond Perruchoud*[1]; Kirstine Hulse[2]; Markus Meier[1]; Werner Fischer[1]; [1]R&D Carbon, Ltd., Sierre 3960 Switzerland; [2]Alusaf Empageni S. Africa

A worldwide survey made on aluminium smelter supplies provided valuable information on the typical values and specifications for coal tar pitch based binders. An overview of ISO analytical standards used for characterizing pitch is given. The evaluation of the last decodes in the coke oven and tars distillers industry is addressed. The future requirements of the Al-industry are discussed.

**9:45 AM**
**Change of Focus: Use of Refinery Simulation Tools for Coke Quality Related Predictions**: *Eberhard Lucke*[1]; [1]KBC Advanced Technologies, Inc., Process Consulting, 580 Westlake Park Blvd., Ste. 1150, Houston, TX 77082 USA

Simulation models help to optimize refineries and petrochemical plants. The same principle can be used to optimize the anode grade coke chain. Potential benefits of this application are increased process efficiency, reduced energy consumption and reduced raw material cost. This paper discusses the results of using a standard Delayed Coker model to predict coke related quality parameters and the effect of process changes on these parameters. Besides a representative anode grade base case the following case studies are analyzed: -Decreased Recycle Ratio -Decreased Drum Pressure -Ramped Coil Outlet Temperature -Blending of 5% S+ Crude Oil. The predicted impact on yield structure, energy consumption and product qualities is presented. The possibility of using the coke quality data with commonly known correlations to estimate calcined coke qualities is evaluated. The discussion of these results shows the gap to best practice and leads to necessary measures for improvement.

**10:10 AM Break**

**10:20 AM**
**Importance of Granulometry in Calcined Petroleum Coke**: *Ravindra Narayan Narvekar*[1]; Ajit Sambhaji Sardesai[1]; Asht B. Prasad[1]; [1]Goa Carbon, Ltd., Production, Dempo House, Campal, Panaji, Goa 403001 India

Goa Carbon Limited, flagship company of DEMPO group, is one of Indiaís largest calciners having three rotary kilns in India and wide customer network across the globe. GCL has sieved out different grain sizes from one CPC lot and analysed the same for purity, structure and porosity parameters. This exercise has been repeated for different origin CPC lots with widely varying sulphur content. It has been observed that there is significant variation in chemical composition for different grain sizes belonging to same CPC lot indicating that some of the impurities have tendency to concentrate in finer grains. Significant variation in the structure and porosity parameters also seen among different grain sizes of same CPC lot indicating difference in Calcination levels undergone by them under otherwise identical conditions. These findings are utilised as a tool to emphasize proper sample preparation especially when sieving, crushing, grinding operations are involved.

**10:45 AM**
**Classification of Pores in Prebake Anodes Using Automated Optical Microscopy**: *Lorentz Petter Lossius*[1]; Stein R□rvik[2]; Harald A. ÿye[3]; [1]Hydro Aluminium Teknologisenter ≈rdal, PO Box 303, ÿvre ≈rdal N-6882 Norway; [2]SINTEF Applied Chemistry, Sem SÊlands veg 12, Trondheim N-7465 Norway; [3]Norwegian University of Science and Technology, Dept. of Chem., Sem SÊlands veg 12, Trondheim N-7491 Norway

The porosity influences anode properties as strength and reactivity. There are several identifiable types of pores; the most important are calcination cracks and gas bubble pores in the petrol coke and mixing and baking pores formed during production. An automatic image analysis method for classification has been developed to allow separate quantification of these different types of pores. The paper will present the method and show examples of pore distributions in green and baked anodes, dependent on recipe, pitch level, vibration forming parameters and process temperatures. It is especially useful to quantify the mixing porosity to study effects of the production process.

**11:10 AM**
**Anode Quality Improvements at the Valesul Smelter**: *Gustavo Franca*[1]; Carlos Mesquita[2]; Les Edwards[3]; [1]Valesul Aluminio S/A, Carbon Plant, Estr. Aterrado do Leme, 1225-Sta. Cruz, Rio de Janiero 23579-900 Brazil; [2]Billiton; [3]CII Carbon, LLC, 700 Coke Plant Rd., Chalmette, LA 70044 USA

Valesul Aluminio S/A is a 93,000 tonne per year smelter located in the suburbs of Rio de Janeiro, Brazil. Historically, Valesul has used a low sulfur petroleum coke for anode manufacture. In a drive to improve anode quality and performance, Valesul started an experiment in 2001 to evaluate the cost and potential benefits associated with using an alternative, higher sulfur coke. The paper describes the methodology and results of a four month plant trial, which simultaneously produced low and high sulfur anodes. High and low sulfur anodes were sent into two different sectors of the potline. Improvements in both anode quality and potline performance demonstrated the significant benefits possible when switching coke qualities in a smelter. Valesul is now evaluating the capital cost and return on a project which would increase its coke storage capacity and allow it to run with a blend of low sulfur and high sulfur cokes.

## Cast Shop Technology: DC Casting II

*Sponsored by:* Light Metals Division, LMD-Aluminum Committee
*Program Organizers:* Jean-Pierre Martin, Aluminum Technologies Centre, c/o Industrial Materials Institute, Boucherville, QC J4B 6Y4 Canada; David H. DeYoung, Alcoa Inc., Alcoa Technical Center, Alcoa Center, PA 15069 USA; Seymour G. Epstein, The Aluminum Association, Inc., Washington, DC 20006 USA; Paul Crepeau, General Motors Corporation, MC/486-710-251, Pontiac, MI 48340-2920 USA

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| Tuesday AM | Room: 6C |
| March 4, 2003 | Location: San Diego Convention Center |

*Session Chairs:* Christian Pluchon, Pechiney Group, Voreppe 38341 France; Laurens Katgerman, Delft University of Technology, Fac. of Cheml. Eng. & Matls. Sci., Delft 2628 AL Netherlands

**8:30 AM Cancelled**
**Evaluation of Commercial CFD Packages Used in Mathematical Modeling of Direct Chill Casting of Aluminum Alloys**: *Daniel Paul Cook*[1]; Christopher Thompson[1]; [1]Virginia Commonwealth University, Mechl. Eng. Dept., 601 W. Main St., PO Box 843068, Richmond, VA 23284-3068 USA

**8:55 AM**
**Modelling of Fluid Flow Phenomena During DC Casting of Aluminium Alloys**: *Laurens Katgerman*[1]; Bart Venneker[2]; Jan Zuidema[2]; [1]Delft University of Technology, Lab. of Matls., Rotterdamseweg 137, Delft, ZH 2628 AL The Netherlands; [2]Netherlands Institute for Metals Research, Rotterdamseweg 137, Delft, ZH 2628 AL The Netherlands

The major drive for casting modelling is to improve the insight how process parameters affect casting performance, in order to prevent casting defects. Reliable calculations of macrosegregation during casting of alloys depend on accurate modelling of the associated physical mechanisms. In solving the solute concentration equation, the accuracy of the velocity field is thus of great concern. Several discretisation schemes for the convection terms are examined on their ability to correctly predict macrosegregation. The occurrence of oxides can give major problems during aluminium casting and processing. During transfer from conventional metal treatment systems to the casting station pick up of inclusions can occur. In our simulations, we have assessed quantitatively some of the upstream fluid flow effects in relation to filling behaviour of the DC mould cavity and number of inclusions trapped in the launder system. Results of numerical simulations of fluid flow with discrete particles of different mass and distribution are given.

**9:20 AM**
**Detailed Modelling of a Metal Distributor by Means of a Combined Numerical and Physical Approach**: *RenÈ Kieft*[1]; Sjaak van Oord[1]; Ferry Frinking[1]; Dico Bal[1]; Hugo van Schoonevelt[1]; [1]Corus RD&T, PB 1000, IJmuiden 1970 CA The Netherlands

During the VDC casting process of ingots, the metal flow into the mould is mostly distributed by using a glass cloth distributor. The design of the distributor strongly determines the generated flow pattern within the liquid pool and this on its turn effects the ingot properties after solidification. For an accurate prediction of the flow pattern in the liquid pool it is necessary to model the flow through the distributor very precisely. Furthermore, the flexible character of the distributor bag demands for taking into account the deformation of the distributor caused by the flow. In most cases such a detailed modelling is unfeasible. Therefore the 3D velocity field at the outflow ports of the distributor was measured by means of an advanced measuring technique called Particle Image Velocimetry. The measurements were performed within a water model. The measured distributor outflow data was then used as inlet boundary conditions in the numerical fluid flow model. The results show that the details of the flow caused by the flexible distributor bag could be captured accurately. The influence of these details on the flow characteristics within the sump are elucidated by comparing the results with calculations in which the distributor was fully modelled. From the results it can be concluded that for a valid prediction of the flow patterns in the sump it is obligatory to incorporate all details caused by the flexible distributor bag.

9:45 AM

**Effect of Water Quality and Water Type on the Heat Transfer in DC Casting**: *Laszlo I. Kiss*[1]; Thomas Meenken[1]; Andre Charette[1]; Yves Lefebvre[2]; Robert LÈvesque[3]; [1]UniversitÈ du QuÈbec ‡ Chicoutimi, DSA, 555 Blvd. de líUniversitÈ, Chicoutimi, Quebec G7H 2B1 Canada; [2]BetzDearborn Canada, Inc., 3451 Erindale Station Rd., Mississauga, Ontario L5A 3T5 Canada; [3]Alcoa Aluminium Smelter in Baie-Comeau, 100, rte. Maritime, Baie-Comeau, Quebec G4Z 2L6 Canada

In the recent years many efforts have been directed toward the analysis of the influence of surface roughness, surface quality water temperature and composition on the heat transfer coefficients between the solidifying ingot and cooling water during the secondary cooling in DC casting. An experimental technique was developed earlier to follow closely the variations of the surface heat flux without modifying the surface properties of the solid. The method was used to analyze the effects of the type and composition of water and that of the cleanliness of the solid surface on the heat extracting capacity of the cooling water.

10:10 AM Break

10:20 AM

**Thermomechanical Analysis of the DC Casting Start-Up Phase for AA5182**: *Neill J. McDonald*[1]; Joydeep Sengupta[2]; Mary A. Wells[2]; Daan M. Maijer[2]; [1]Carnegie Mellon University, Dept. of Matls. Sci. & Eng., 5000 Forbes Ave., Pittsburgh, PA 15232 USA; [2]University of British Columbia, Dept. of Metals & Matls. Eng., 309-6350 Stores Rd., Vancouver, BC V6T 1Z4 Canada

Recently thermo-mechanical finite element (FE) models based on fundamental principles have emerged as powerful tools to predict the temperature distribution and stress-strain fields in the solidifying aluminum ingot during the Direct Chill (DC) casting process. A critical aspect of these process models, is the way the constitutive behaviour of the material is modeled in the solid state as this can influence the stress, strain and butt curl predictions during the casting process. This paper compares four different methods of modelling constitutive behaviour, in the solid state, available in the commercial FE package, ABAQUS, namely: elastic-plastic, elastic-rate dependent plastic, creep, and combined creep and rate dependent plastic using data measured on as-cast AA5182 at strain rates and temperatures consistent with those typically seen during DC casting. The comparison of the different methods was done using a 2-D uncoupled axisymmetric thermal and stress model of an aluminum billet during the start-up phase of the DC casting process.

10:45 AM

**Computing Free Surface Film of Liquid Metal During Mould Filling**: *Jiawei Mi*[1]; [1]The University of Birmingham, Sch. of Eng., IRC in Matls. Procg., Elm Rd., Edgbaston, Birmingham, England B15 2TT UK

The mould filling of gravity top pouring and tilt pouring of an Al-4.5% Cu alloy has been studied by using a real-time X-ray video radiography system and a computational fluid dynamic code (Flow 3D). The liquid metal flow exhibited tranquil, turbulent or very chaotic phenomena due to the different filling conditions used in the experiment. The moving free surface of liquid metal was accurately tracked and various flow features were precisely presented by modeling. Based on an optimized filling sequence (free from surface turbulence), a method was developed to quantify the potentially entrained free surface film for the mould fillings that experienced free surface turbulence. The defects of the castings which experienced different filling phenomena were measured and analyzed. It revealed that the increase of the potentially entrained surface film resulted in the monotonous increase of the number and the average size of the defects in the castings.

11:10 AM

**Mathematical Modelling of Water Ejection and Water Incursion During the Start-Up Phase of the DC Casting Process**: *J. Sengupta*[1]; D. Maijer[1]; M. A. Wells[1]; S. L. Cockcroft[1]; A. Larouche[2]; [1]University of British Columbia, Metals & Matls. Eng., 309-6350 Stores Rd., Vancouver, BC V6T 1Z4 Canada; [2]Alcan International Ltd., Arvida R&D Ctr., 1955 Mellon Blvd., PO Box 1250, Jonquiere, Quebec G7S 4K8 Canada

A comprehensive mathematical model has been developed to describe heat transfer during the start-up phase of the Direct Chill casting process. This 3-D thermal model, based on the commercial finite element package ABAQUS, includes primary cooling to the mould, secondary cooling to water and ingot base cooling. The algorithm used to account for secondary cooling to water includes boiling curves that are a function of surface temperature, water flow rate and position relative to the point of water impingement. Based on experimental measurements and observations, the algorithms used to describe secondary cooling and ingot base cooling have been augmented to include the physical phenomena of water ejection from the ingot surface and water incursion between the ingot base and bottom block surface. The model has been validated against temperature measurements obtained from two 711 x 1680 mm AA5182 ingots, cast under different conditions (non-typical ìcoldî practice and non-typical ìhotî practice). Comparison of the model predictions with the thermocouple data indicates that this 3-D thermal model correctly describes the heat flow in the early stages of the casting process throughout the ingot and bottom block.

11:35 AM

**Understanding DC-Cast Microstructures Using Laboratory-Based Solidification Techniques**: *Mike William Meredith*[1]; [1]Alcan International Ltd., Banbury Labs., Southam Rd., Banbury, Oxon OX16 2SP UK

Many of the microstructural features that exist in a DC-cast Al alloy ingot survive subsequent processing steps and contribute to the final properties of the product. For example, the formation of constituent particles may affect ìfir-treeî generation and, hence, surface quality in commercial purity alloys and downstream texture development in beverage can sheet. It is important, therefore, to understand which of the microstructural features generated during solidification are most important and, where feasible, how to control or influence them. Investigating commercially produced material, however, is expensive so it is becoming increasingly important to study solidification microstructure formation from within the laboratory. To this end, there are a number of tools available (for example, controlled directional solidification, DC-casting simulation, laboratory scale DC-casting, numerical simulations). This paper aims to assess how accurate and reliable such methods are and the precautions that should be taken when comparing the results of these to full-scale DC-cast material.

## Computational Methods in Materials Education: New Computational Courses

*Sponsored by:* TMS-Education Committee

*Program Organizers:* Zi-Kui Liu, Pennsylvania State University, Materials Science and Engineering, State College, PA 16082-5006 USA; Mark D. Asta, Northwestern University, Department of Materials Science and Engineering, Evanston, IL 60208-3108 USA; Long-Qing Chen, Pennsylvania State University, Materials Science and Engineering Department, University Park, PA 16802-5005 USA

Tuesday AM — Room: 13
March 4, 2003 — Location: San Diego Convention Center

*Session Chair:* Mark D. Asta, Northwestern University, Dept. of Matls. Sci. & Eng., Evanston, IL 60208-3108 USA

8:30 AM Invited

**Graduate Course in Materials Modeling at Princeton**: *David J. Srolovitz*[1]; [1]Princeton University, Princeton Matls. Inst., 70 Prospect Ave., Bowen Hall, Princeton, NJ 08544-5211 USA

Computational Materials Modeling is a regular graduate course for first year graduate students at the Princeton Materials Institute. It is designed to familiarize the graduate students with a wide range of simulation methodologies from first-principles to atomistic to microstructural to continuum. The course focuses on understanding the methods such that each student is able to write a simple computer simulation code. During this course, the students are assigned four projects which require them to write their own simulation codes. I will discuss the philosophy of the computer simulation course, the subject matter covered, as well as the mechanisms employed to make it possible for students to write their own simulation codes.

9:00 AM Invited

**Introduction to Modeling and Simulation: A Multidisciplinary Approach to Computational Materials Education**: *Adam C. Powell*[1]; Sidney Yip[2]; [1]Massachusetts Institute of Technology, Dept. of Matls. Sci. & Eng., 77 Massachusetts Ave., Rm. 4-117, Cambridge, MA 02139-4301 USA; [2]Massachusetts Institute of Technology, Dept. of Nucl. Eng., 77 Massachusetts Ave., Rm. 24-208, Cambridge, MA 02139-4301 USA

Introduction to Modeling and Simulation, first taught in Spring 2002, is a broad overview of computation for processing-structure-property relationships. This subject draws lecturing faculty from the

TUESDAY AM

departments of Materials Science and Engineering, Nuclear Engineering, Applied Mathematics, Civil and Environmental Engineering, Health Sciences and Technology and Chemical Engineering, with undergraduate and graduate student representation from a similar diversity of backgrounds. First half lectures cover modeling methodologies with assignments spanning lengthscales from electronic structure of simple molecules, to percolation clusters, to Ising models, to finite difference modeling of heat conduction and phase change. Students spend the second half working on term projects, with lectures covering recent research breakthroughs making use of methodologies taught in the first half. This talk will focus on experiences in managing the diverse backgrounds of students and faculty, both in terms of differences in approach between departments, and also varying mathematical and computational backgrounds of the students.

**9:30 AM Invited**
**A New Course Integrating Computational and Experimental Methods in Materials Engineering**: *James B. Adams*[1]; Shahriar Anwar[2]; [1]Arizona State University, Cheml. & Matls. Eng., PO Box 876006, Tempe, AZ 85287-6006 USA

In response to feedback from our Advisory Board, we created a new course, MSE 394 Computational and Experimental Methods in Materials Engineering. This course is intended to follow our introductory materials course. The course was intended to provide students with an integration of experimental and computational skills, as will be expected by future employers. This course includes an introduction to Fortran programming, UNIX, LabView programming/data acquisition, crystal building/modeling, OOF (microstructure evaluation and mechanical behavior modelling), Design of Experiments (concrete optimization), 4-point probe measurements, and magnetic bubble behavior. Throughout the course, computational and experimental methods are integrated as much as possible.

**10:00 AM Break**

**10:30 AM Invited**
**Object Oriented Finite Element Modeling (OOF) of Microstructures in a New Course in Materials Engineering**: *Shahriar Anwar*[1]; James B. Adams[1]; Nikhilesh Chawla[1]; [1]Arizona State University, Cheml. & Matls. Eng., Tempe, AZ 85287-6006 USA

We are teaching a new course entitled Computational and Experimental Methods in Materials Engineering aimed at the sophomore/junior level in materials engineering. One of the topics covered in this course is microstructure-based simulation using finite element analysis techniques. The tool that we use is a public domain software called OOF (Object Oriented Finite Element) developed at the National Institute of Science & Technology (NIST). We will discuss our implementation of OOF in this course, as well as improvements and ongoing development based on feedback from our students.

**11:00 AM Invited**
**Incorporating Computational Materials Research into Graduate Courses: A Hands-On Approach**: *Diana Farkas*[1]; [1]Virginia Tech, Matls. Sci. & Eng., Blacksburg, VA 24061 USA

We describe a hands on approach to incorporating computational materials research into the graduate curriculum. The approach involves the students actually using atomistic simulation codes as a homework tool. The approach has been used in a graduate course on computational techniques in materials science, and is also appropriate as a teaching tool in other courses, such as dislocation theory, and fracture mechanics. The examples used involve calculations ranging from simple defects, such as surface energies and simple vacancies to dislocation core structure and simulations of fracture.

**11:30 AM Invited**
**Facing the Challenge of Biological Materials: From DNA to Self-Assembled Bilayers**: *Rob Phillips*[1]; [1]Caltech, Div. of Eng. & Appl. Sci., 1200 E. California Blvd., Pasadena, CA 91125 USA

Model building in materials science is a crucial element of the drive to construct a new generation of materials based upon fundamental understanding as opposed to enlightened empiricism. One class of materials of ever increasing importance is that of ìbiological materialsî ranging from the synthesis of artificial proteins to the exploitation of molecular motors and beyond. Successful use of this broad class of materials represents a truly interdisciplinary endeavor and poses intriguing challenges from the standpoint of education since it draws from biology, chemistry, physics, materials science and other domains as well. This talk will examine some of the beautiful models that have been set forth recently to respond to experiments in single molecule biology and to show how such models (and their computational incarnations) and the associated experiments can be brought to the classroom setting.

## Computational Phase Transformations: Fundamental Properties of Surfaces and Interfaces

*Sponsored by:* ASM International: Materials Science Critical Technology Sector, Electronic, Magnetic & Photonic Materials Division, Structural Materials Division, Materials Processing & Manufacturing Division, ASM/MSCTS-Thermodynamics & Phase Equilibria Committee, MPMD-Computational Materials Science & Engineering-(Jt. ASM-MSCTS), Jt. EMPMD/SMD-Chemistry & Physics of Materials Committee, Phase Transformation Committee-(Jt. ASM-MSCTS)
*Program Organizers:* Yunzhi Wang, The Ohio State University, Department of Materials Science and Engineering, Columbus, OH 43210 USA; Perry Leo, University of Minnesota, Department of Aerospace Engineering and Mechanics, Minneapolis, MN 55455 USA; Ralph E. Napolitano, Iowa State University, Ames Laboratory, Department of Materials Science and Engineering, Ames, IA 50011 USA; Vidvuds Ozolins, Sandia National Laboratories, Livermore, CA 94551-0969 USA; Wolfgang Windl, The Ohio State University, Department of Materials Science and Engineering, Columbus, OH 43210 USA

Tuesday AM — Room: 11B
March 4, 2003 — Location: San Diego Convention Center

*Session Chairs:* Wolfgang Windl, The Ohio State University, Dept. of Matls. Sci. & Eng., Columbus, OH 43210 USA; Jeffrey J. Hoyt, Sandia National Laboratories, Matls. & Process Modlg., Albuquerque, NM 87122 USA

**8:30 AM Invited**
**Accelerated Molecular Dynamics**: *Arthur F. Voter*[1]; [1]Los Alamos National Laboratory, Theoretl. Div., MS B268, Los Alamos, NM 87545 USA

A significant problem in the atomistic simulation of materials is that molecular dynamics simulations are limited to nanoseconds, while important reactions and diffusive events often occur on time scales of microseconds and longer. Although rate constants for slow events can be computed directly using transition state theory (with dynamical corrections if necessary), this requires first knowing the transition state. Often, however, we cannot even guess what events will occur. For example, in vapor-deposited metallic surface growth, surprisingly complicated exchange events are pervasive. I will discuss recently developed methods (hyperdynamics, parallel replica dynamics, and temperature accelerated dynamics) for treating this problem of complex, infrequent-event processes. The idea is to directly accelerate the dynamics to achieve longer times without prior knowledge of the available reaction paths. I will present our latest method developments and some recent applications, including metallic surface growth and deformation of carbon nanotubes.

**9:00 AM Invited**
**Computing the Kinetic Coefficient in Solid-Liquid Systems from Molecular Dynamics Simulations**: *Jeffrey J. Hoyt*[1]; Deyun Sun[2]; Mark D. Asta[2]; Alain Karma[3]; [1]Sandia National Laboratories, Matls. & Process Modlg., Bldg. 897, MS 1411, Albuquerque, NM 87122 USA; [2]Northwestern University, Dept. of Matls. Sci. & Eng., Robert R. McCormick Sch. of Eng. & Appl. Sci., 2225 N. Campus Dr., Evanston, IL 60208 USA; [3]Northeastern University, Physics Dept., 111 Dana Rsrch. Ctr., 110 Forsyth St., Boston, MA 02115 USA

The kinetic coefficient is the constant of proportionality between the velocity of a solid-liquid interface and the interface undercooling. The value of the kinetic coefficient and its dependence on growth direction are critical parameters in continuum modeling of dendritic solidification. In the present work three methods of extracting the kinetic coefficient from molecular dynamics simulations will be discussed. The technique of fluctuation kinetics tracks fluctuations of the solid-liquid interface for a system maintained at the melting point. A correlation function describing the time dependence of the k-space fluctuation amplitude can then be used to derive the kinetic coefficient. A second method, free solidification, employs constant NPT simulations and monitors the interface position as a function of time. The free solidification technique will be discussed paying particular attention to the means by which pressure is controlled. Finally, the imposed pressure technique employs solid-liquid systems main tained at the melting point, but with high pressures applied normal to the interface. The pressure induced undercooling is obtained from the Clausius-Claperyon relation. All three techniques will be compared for the case of pure Ni modeled using interatomic potentials of the embedded atom type and rapid solidification simulations will be used to study the phenomenon of disorder trapping in Ni-Al alloys.

**9:30 AM Invited**

**Atomistic Simulations of Alloy Solid-Liquid Interfaces**: *Mark D. Asta*[1]; Deyan Sun[1]; Jeffrey J. Hoyt[2]; Alain Karma[3]; [1]Northwestern University, Dept. of Matls. Sci. & Eng., Evanston, IL 60208-3108 USA; [2]Sandia National Laboratories, Albuquerque, NM 87122 USA; [3]Northeastern University, Boston, MA 02115 USA

We demonstrate the application of Molecular-Dynamics and Monte-Carlo simulation methods to the calculation of solid-liquid interface properties relevant for the evolution of solidification microstructure in metallic alloys. Interfacial free energies, and their associated crystalline anisotropies, are computed from capillary fluctuation spectra derived from equilibrium molecular-dynamics simulations. We further discuss how interface mobilities in alloy systems can be extracted from analyses of capillary-fluctuation relaxation kinetics. These approaches are applied to studies of solid-liquid interface properties in both Cu-Ni and Al-Cu alloy systems modeled by many-body interatomic potentials of the embedded-atom form. In order to examine effects of solute upon both kinetic and thermodynamic interface properties, calculated results for alloys are compared in both cases to corresponding values in the associated pure solvent materials.

**10:00 AM Break**

**10:15 AM Invited**

**Direct Calculations of Crystal-Melt Interfacial Free Energies for Simple Materials**: *Brian B. Laird*[1]; [1]University of Kansas, Chem., 1251 Wescoe Hall Dr., Lawrence, KS 66045 USA

Using a recently developed molecular-dynamics simulation method [Davidchack and Laird, Phys. Rev. Lett. 85,4751 (2000)], we determine the crystal-melt interfacial free energy for the hard-sphere and Lennard-Jones model systems as functions of interfacial orientation.In addition, it is shown that Turnbullís rule for the crystal-melt interfacial free energy of close packed metals can be explained with quantitative accuracy solely using the hard-sphere model, indicating that this quantity is primarily entropic in origin.

**10:45 AM Invited**

**The Dependence of the Anisotropic Solid-Liquid Interfacial Free Energy on Interatomic Potentials**: *James R. Morris*[1]; Xueyu Song[2]; [1]Iowa State University, Ames Lab., USDOE, Metal & Ceram. Scis., Ames, IA 50011 USA; [2]Iowa State University, Dept. of Chem., 303 Wilhelm, Ames, IA 50011 USA

We have calculated the orientation dependence of the solid-liquid free energy, examining the effect of interatomic potentials. The free energy calculation examines the equilibrium fluctuations of the interface, using molecular dynamics simulations of the coexisting phases. The interfacial free energy of aluminum was calculated using both the Embedded Atom Method potentials of Ercolessi and Adams, and of Mei and Davenport, with the modification from Sturgeon and Laird. We compare the results with each other and with experimental results, and also compare the liquid structure calculated using these potentials with experimental results. We have also examined the interfacial free energy in a number of model systems, including the Lennard-Jones interaction and purely repulsive systems, to see how changing the potential affects the interfacial properties. Finally, we will present preliminary results on the direct calculation of the free energies of the solid and liquid phases, using a modified Weeks-Chandler-Anders on approach that eliminates the need for simulations, and explore the possibility of a similarly direct calculation of the interfacial free energy.

**11:15 AM Invited**

**Interface Modeling**: Chao Jiang[1]; Long-Qing Chen[1]; *Zi-Kui Liu*[1]; [1]The Pennsylvania State University, Dept. of Matls. Sci. & Eng., University Park, PA 16802 USA

The key issue in integrating bulk thermodynamic/kinetic modeling and kinetic simulation is the modeling of interfaces separating two phases of the same structure or different structures. In this presentation, various interface modeling techniques will be reviewed and discussed in the frame work of the interface types, thermodynamic models, thermodynamics of solute segregation, and migration of interfaces. Particular attention will be paid to the integration of the CALPHAD-type thermodynamic and kinetic modeling with the phase-field-type diffuse interface.

TUESDAY AM

## Defects and Deformation of Crystalline Solids - in Honor of Dr. Man H. Yoo - III

*Sponsored by:* ASM International: Materials Science Critical Technology Sector, Electronic, Magnetic & Photonic Materials Division, Structural Materials Division, Jt. EMPMD/SMD-Chemistry & Physics of Materials Committee, SMD-Mechanical Behavior of Materials-(Jt. ASM-MSCTS), SMD-Physical Metallurgy Committee

*Program Organizers:* Jong K. Lee, Michigan Technological University, Metallurgical & Materials Engineering Department, Houghton, MI 49931-1200 USA; Sean R. Agnew, University of Virginia, Materials Science and Engineering Department, Charlottesville, VA 22904-4745 USA; K. N. Subramanian, Michigan State University, Department of Material Science & Mechanics, East Lansing, MI 48824-1226 USA

Tuesday AM — Room: 17A
March 4, 2003 — Location: San Diego Convention Center

*Session Chairs:* David Srolovitz, Princeton University, Mechl. & Aeros. Eng., Princeton, NJ 08544 USA; Hamish Fraser, Ohio State University, Dept. of Matls. Sci. & Eng., Columbus, OH 43210 USA

**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]; [1]University of Pennsylvania, Dept. of Matls. Sci. & Eng., 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 an d 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.

**8:55 AM**

**Dislocation-Solute Atom Interactions in Mo-W and Ta-W Alloys Studied by a Kinetic Monte Carlo Model**: *Chaitanya S. Deo*[1]; David J. Srolovitz[1]; Wei Cai[2]; Vasily V. Bulatov[2]; [1]Princeton University, Mechl. & Aeros. Eng., Princeton, NJ 08544 USA; [2]Lawrence Livermore National Laboratory, Chem. & Matls. Sci., Livermore, CA 94550 USA

Crystal plasticity in metals and alloys depends on the nature of interactions between dislocations and solutes in addition to the dislocation behavior that is present in pure metals. Dislocation Dynamics (DD) simulations require mobility laws that prescribe the behavior and velocity of a dislocation as a function of solute concentration, temperature and applied stress. We present a kinetic Monte Carlo (kMC) simulation of the glide of a single <111> oriented screw dislocation on the (011) plane in Mo and Ta in the presence of substitutional tungsten (W) atoms. The kMC simulation is used to develop mobility laws prescribing the dependence of the dislocation velocity on the driving force and on the inhibiting lattice and solute resistance. The W atoms are substitutional impurities distributed in three dimensions around the screw dislocation and create a small distortion in the Ta and Mo lattice. Both short range and long range solute-dislocation interactions are included in the model. The dislocation motion is r epresented by the kink model, which explicitly includes double kink nucleation, kink migration and kink-kink annihilation. We integrate over the initial evolution of the embryonic double kink by treating the double kink as a one-dimensional random walker and obtaining the distribution of the elapsed time before the double kink stabilizes. Incorporation of such a double kink nucleation model is a key to efficient simulations. The dislocation velocity shows an Arrhenius dependence on the temperature as the double kink nucleation process is thermally activated. The solutes inhibit the motion of the dislocation, leading to a reduction in the dislocation velocity, also called dislocation friction.

**9:15 AM Invited**

**Strain Hardening by Mesoscale Simulations**: *Ladislas P. Kubin*[1]; [1]LEM, CNRS-ONERA, 29 Av. de la Division Leclerc, BP 72, 92322 Chatillon, Cedex France

Strain hardening can be decomposed into a product of two contributions. One is due to forest hardening that relates the flow stress to dislocation densities, the other stems from the evolution of dislocation densities with time. In order to establish a relation with the continuum modelling of plastic deformation, strain hardening is expressed in the form of a matrix, whose components describe how the critical stress in one slip system depends on the plastic strain in other systems. The way dislocation dynamics simulations can contribute to remove arbitrariness in the definition of the hardening matrix is discussed on several examples. Forest hardening, the related interactions between slip systems and the evolutionary laws for dislocation densities are discussed in materials with low and high lattice friction. This will be illustrated for the case of fcc, bcc and hcp crystals.

**9:40 AM**

**In Situ Studies of Deformation by Nanoindentation**: Andrew Minor[1]; Erica T. Lilleodden[1]; Eric A. Stach[2]; *John William Morris*[1]; [1]University of California, Matls. Sci., Evans Hall, Berkeley, CA 94720 USA; [2]Lawrence Berkeley Laboratory, NCEM, 1 Cyclotron Dr., Berkeley, CA 94720 USA

We have used a unique nanoindentation stage mounted on a high-resolution electron microscope at NCEM/LBNL to observe, in situ, the nucleation and development of mechanical deformation during nanoindentation. This talk will focus on the deformation of Al. Indentation in the center of a relatively large grain produces deformation by the spontaneous generation of dislocations, suggesting the ideal behavior of defect-free crystals. Deformation near grain boundaries forces the participation of those boundaries, often through surprisingly large, recoverable excursions. The characteristic deformations will be described, shown and interpreted.

**10:00 AM**

**Anomalous Slip in High-Purity Molybdenum Single Crystals**: *Luke L. Hsiung*[1]; David H. Lassila[1]; [1]Lawrence Livermore National Laboratory, Chem. & Matls. Sci., 7000 East Ave., L-352, PO Box 808, Livermore, CA 94551-9900 USA

Dislocation multiplication and propagation in high-purity Mo deformed by anomalous slip have been investigated. The result reveals that the initial screw dislocations associated with grown-in superjogs can act as effective sources for multiplying 1/2[111] and 1/2[1-11] coplanar screw dislocation arrays in the (-101) primary slip plane. The interaction force between the freshly multiplied 1/2[111] screw dislocations and 1/2[1-11] screw dislocations results in the multiplication of 1/2[1-11] screw dislocations, which leads to the formation of 1/2[111] and 1/2[1-11] cross-grid dislocation arrays in the (-101) primary slip plane. It is proposed that the occurrence of {0-11} anomalous slips is intimately related to the onset of a domino event of dislocation propagation caused by the internal stresses originating from the interactions between the cooperative screw dislocation arrays. The internal stresses render the propagation of 1/2[111] and 1/2[1-11] screw dislocations from the primary slip planes onto the {011} planes by a stress-induced cross-slip process, and subsequently resulting in the anomalous operation of slip systems in the {011} planes. This work was performed under the auspices of the US Department of Energy by University of California Lawrence Livermore National Laboratory under contract No. W-7405-Eng-48.

**10:20 AM Break**

**10:40 AM Invited**

**Computer Simulation of Defect Generation and Properties, and Dislocation-Obstacle Interactions in Metals**: *David John Bacon*[1]; [1]The University of Liverpool, Dept. of Eng., Brownlow Hill, Liverpool L69 3GH UK

Recent advances in areas where computer modelling is being used for research into radiation damage, dislocation-obstacle interactions and twinning in metals will be reviewed. Defect production by displacement cascades, and the numbers and arrangements of point defects in these primary events are now well-understood. An unexpected degree of defect clustering has been revealed, and the mobility of defect clusters has been investigated and shown to play a potentially important role in the evolution of microstructure. Atomic-scale modelling is also being used in realistic simulation of the interaction of dislocations with obstacles such as dislocation loops, voids and precipitates, and the information gained can be used to assist continuum-scale modelling of yield and flow. In the field of twinning, simulation has been used to understand the important role of dislocations in interfacial processes.

**11:05 AM**

**TEM Investigation of Nanoindentation Plastic Zones in an Alpha/Beta Ti Alloy**: *Gopal B. Viswanathan*[1]; Eunha Lee[1]; Hamish L. Fraser[1]; [1]The Ohio State University, Matls. Sci. & Eng., 477 Watts Hall, 2041 College Rd., Columbus, OH 43210 USA

The advent of nanoindentation technique has provided us with the ability to probe a smaller volume of material for mechanical properties such as elastic modulus, yield stress etc. in the areas of thin films, coatings and multiplayer materials etc. In this study, the same technique has been applied to evaluate the mechanical properties of Ti-Al based alloy containing alpha/beta two-phase microstructure. Specifically, nanohardness measurements were obtained from individual alpha and beta phases in these alloys. TEM samples were carefully prepared beneath specific indentations using Focused Ion Beam (FIB) slicing method and the deformation structures from these samples are investigated in detail. Attempts have been made to correlate the trends that are seen in hardness estimates to various microstructural features such as grain size, composition, orientation of individual phases supported by the advent of nanoindentation technique has provided us with the ability to probe a smaller volume of material for mechanical properties such as elastic modulus, yield stress etc. in the areas of thin films, coatings and multiplayer materials etc. In this study, the same technique has been applied to evaluate the mechanical properties of Ti-Al based alloy containing a two-phase ($\alpha+\beta$) microstructure. Specifically, nanohardness measurements were obtained from individual a and b phases in these alloys. TEM samples were carefully prepared beneath specific indentations using Focused Ion Beam (FIB) slicing method and the deformation structures from these samples are investigated in detail. Attempts have been made to correlate the trends that are seen in hardness estimates to various microstructural features such as grain size, composition, orientation of individual phases supported by Orientation Microscopy (OM) and detailed TEM analysis of the deformation structures.

**11:25 AM Invited**

**Anomalous Hardening at High Temperatures in Gamma TiAl**: *Sung H. Whang*[1]; Zhijie Jiao[1]; Qiang Feng[2]; Zhongmin Wang[1]; [1]Polytechnic University, Dept. of Mechl. Eng., Six MetroTech Ctr., Brooklyn, NY 11201 USA; [2]University of Michigan, Dept. of Matls. Sci. & Eng., Inst. of Sci. & Tech., M-13, IST Bldg., H. H. Dow Bldg., 2300 Hayward St., Ann Arbor, MI 48109 USA

Anomalous increase in yield stress at high temperatures has been observed in a number of intermetallics. The micromechanisms for anomalous yield stress in intermetallic alloys such as $L1_2$ $Ni_3Al$ and $Ni_3Ga$ were relatively well known. On the other hand, gamma TiAl exhibits complex dislocation features and diversified cross-slip profiles, which led to potential multiple-pinning mechanisms. Furthermore, the active dislocation types are different in Ti rich gamma TiAl alloys from those in Al rich TiAl alloys, which makes us to evaluate both roles of superdislocations as well as ordinary dislocations in slip. In the past, in addition to the static and dynamic observation of defect structures, theoretical effort based on the change in kink interaction energy in various slip planes has been carry out to understand the pinning mechanisms of active dislocations. In this presentation, we will present some of the experimental results as well as theoretical calculations, and attempt to shed new lights on the subject of anomalous hardening at high temperatures.

**11:50 AM**

**Dynamic Strain Aging and Strength Anomaly of $L1_2$-Type Intermetallic Alloys at Intermediate Temperature**: *Takayuki Takasugi*[1]; Hyabusa Honjo[1]; Yasuyuki Kaneno[1]; Hirofumi Inoue[1]; [1]Osaka Prefecture University, Dept. of Metall. & Matls. Sci., 1-1 Gakuen-cho, Sakai, Osaka 599-8531 Japan

The serrated plastic flow of $L1_2$-type $Co_3Ti$, $Ni_3(Si,Ti)$ and $Ni_3Al$ intermetallic alloys in forms of poly- and single-crystals was investigated at intermediate temperature by tensile tests in terms of the effects of temperature, strain rate, composition and microstructure. The serrated plastic flow and negative strain rate sensitivity was generally observed at intermediate temperature in which positive temperature dependence of the flow stress has been shown. Such plastic instability was correlated with dynamic strain aging. It is suggested that solutes interact with a decomposed screw dislocation in its inelastic strain field, and modify the core structure of a decomposed screw dislocation, resulting in plastic flow instability. In this article, it is discussed how solutes as well as dislocation core structures affect the dynamic strain aging in $L1_2$ intermetallic alloys.

## Dynamic Deformation: Constitutive Modeling, Grain Size, and Other Effects: Symposium in Honor of Professor Ronald W. Armstrong: Shock Compression

*Sponsored by:* Structural Materials Division, ASM International: Materials Science Critical Technology Sector, SMD-Mechanical Behavior of Materials-(Jt. ASM-MSCTS)
*Program Organizers:* Marc Andre Meyers, University of California-San Diego, Department of Mechanical and Aerospace Engineering, La Jolla, CA 92093-0411 USA; George T. Gray III, Los Alamos National Laboratory, Dynamic Properties Team, Los Alamos, NM 87545-0001 USA; Naresh Thadhani, Georgia Institute of Technology, School of Materials Science and Engineering, Atlanta, GA 30332-0245 USA; Kenneth S. Vecchio, UC San Diego, Dept of Mechanical and Aerospace Engineering, La Jolla, CA 92093-0411 USA

Tuesday AM Room: 16B
March 4, 2003 Location: San Diego Convention Center

*Session Chair:* N. N. Thadhani, Georgia Institute of Technology, Matls. Sci. & Eng., Atlanta, GA 30332-0245 USA

**8:30 AM**
**Observations of Common Microstructural Issues Associated with Dynamic Deformation Phenomena: Twins, Microbands, Dynamic Recrystallization, and Grain Size Effects**: *Lawrence E. Murr*[1]; [1]University of Texas at El Paso, Metallurgl. & Matls. Eng., 500 W. University Ave., El Paso, TX 79968-0520 USA

Plane wave shock deformation has been shown to produce deformation twins or twin-faults in essentially all metal and alloys. In FCC metals and alloys twinning depends upon stacking-fault free energy (SFE) and a critical twinning pressure; which increases with increasing SFE. For impact cratering where the shock wave is spherical and a prominent shear stress is involved, metals and alloys with high SFE form microbands coincident with {111} planes while low SFE metals and alloys either form mixtures of twins and microbands or twins. Oblique shock loading of copper also produces mixtures of twins and microbands. Both twins and microbands increase in volume fraction with increasing grain size. BCC iron is observed to twin in both shock loading and as a result of impact cratering. Impact craters, shaped charges, and other examples of extreme deformation and flow at high strain rates exhibit dynamic recrystallization as a mechanism of solid-state flow. Deformation twins are also often precursors to this process as well. Examples of these phenomena in FCC materials such as Al, Ni, Cu, stainless steel and brass and BCC materials such as W, Mo, W-Ta, Ta will be presented; with emphasis on transmission electron microscopy.

**9:00 AM**
**Materials Science Under Extreme Conditions of Pressure and Strain Rate**: *Bruce A. Remington*[1]; Grant Bazan[1]; Eduardo M. Bringa[1]; Maria J. Caturla[1]; M. John Edwards[1]; Daniel H. Kalantar[1]; Mukul Kumar[1]; Barbara F. Lasinski[1]; K. Thomas Lorenz[1]; James M. McNaney[1]; Stephen M. Pollaine[1]; David B. Reisman[1]; James S. Stolken[1]; Justin S. Wark[2]; Barukh Yaakobi[3]; [1]Lawrence Livermore National Laboratory, Y-Div., HED Prog., PO Box 5001, Livermore, CA 94551-9970 USA; [2]University of Oxford, Oxford UK; [3]University of Rochester, Lab. for Laser Energetics, Rochester, NY USA

Solid state experiments at very high pressures and strain rates are possible on high power laser facilities, albeit over brief intervals of time and small spatial scales. Bragg diffraction on single-crystal surrogates and VISAR measurements establish the ultrahigh strain rates of $10^7$-$10^8$ $s^{-1}$. Solid-state strength is inferred using the Rayleigh-Taylor instability as a ìdiagnosticî. Temperature and compression in polycrystalline samples can be deduced from EXAFS measurements. Deformation mechanisms can be identified by examining recovered samples. We will briefly review this new area of laser-based materials science research, then present a path forward for carrying these solid-state experiments to much higher pressures, P > 10 Mbar, on the NIF laser facility. This work was performed under the auspices of the US Department of Energy by the Lawrence Livermore National Laboratory under Contract No. W-7405-ENG-48.

**9:30 AM**
**Simulating Shock Propagation in Single Crystal Cu and Al**: *Eduardo Marcial Bringa*[1]; Paul Erhart[1]; Nicolai Tanushev[1]; Maria Jose Caturla[1]; Brian D. Wirth[1]; Dan Kalantar[1]; James Stolken[1]; [1]Lawrence Livermore National Laboratory, Chem. & Matl. Scis., PO Box 808, L-353, Livermore, CA 94551 USA

Large scale molecular dynamics simulations with the embedded atom method (EAM) potentials are used to simulate shock propagation in single crystal Cu and Al for different crystal orientations. Simulations were performed for a wide pressure range (2-300 GPa) and agree well with existing experimental data for both metals. Large anisotropies are found for shock propagation in Cu, with different plasticity mechanisms along different directions. Experiments for ìsingle crystalsî deal with samples having a small initial defect density, including point defects, dislocations, etcetera. Therefore, simulations were also run for crystals with vacancies and nano-void distributions before the shocks. The effect of the defects on the Hugoniot, the Hugoniot elastic limit and the resulting plastic deformation will be discussed. This work was performed under the auspices of the US Department of Energy by the University of California, Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

**9:45 AM**
**High Strain Rate Deformation and Failure in Pre-Shocked Metals**: *Geoffrey H. Campbell*[1]; James M. McNaney[1]; Mukul Kumar[1]; James S. Stolken[2]; F. Xabier Garaizar[3]; [1]Lawrence Livermore National Laboratory, Chem. & Matl. Sci. Direct., PO Box 808, MS L-356, Livermore, CA 94550 USA; [2]Lawrence Livermore National Laboratory, Eng. Direct., PO Box 808, L-342, Livermore, CA 94550 USA; [3]Lawrence Livermore National Laboratory, Ctr. for Appl. Scientific Compu., PO Box 808, MS L-561, Livermore, CA 94550 USA

Deformation microstructure evolution is a controlling aspect of metal dynamics in general and many types of failure observed in practice. There are large bodies of scientific information on both microstructural evolution and failure of ductile metals that start with a low defect density; however, less is known about highly defective metals. Shocks induce deformation microstructures with high dislocation densities that are comprised, for the most part, of statistically stored dislocations. This highly defective state allows recovery mechanisms to begin at an earlier point in the deformation behavior, reducing the work hardening rate and increasing the propensity for shear localization. We have induced shocks using laser drives in pure Ta, Ta - 2.5% W alloy, and pure Cu under a variety of conditions. We have measured their mechanical properties and characterized their microstructures in the pristine, shock processed and mechanically strained conditions with a variety of techniques, including EBSD mapping and TEM. We have also performed plane stress fracture mechanics tests with the double edge notched tension specimen. The mechanical response will be discussed in terms of the observed deformation microstructures. This work performed under the auspices of US Department of Energy by University of California, Lawrence Livermore National Laboratory under contract no. W-7405-Eng.-48.

**10:00 AM**
**Atomistic Modeling of Spherical Shocks in Single and Nanocrystalline Copper**: *Maria J. Caturla*[1]; Alison Kubota[1]; James S. St^lken[1]; James M. McNaney[1]; Bruce A. Remington[1]; Tomas Diaz de la Rubia[1]; [1]Lawrence Livermore National Laboratory, Chem. & Matls. Sci., L-353, PO Box 808, Livermore, CA 94550 USA

Shock propagation has traditionally been studied using continuum models. However, under certain geometries, the boundary conditions can have an impact in the solutions obtained. Such a situation arises when studying spherical shocks. One way of overcoming this limitation is to use molecular dynamics simulations. We have studied the effect of spherical shocks with peak stresses between 5 and 40GPa on a copper target. The initial condition is a copper sphere 35 to 82nm in diameter. The influence of grain boundaries on shock propagation and energy dissipation is studied in nanocrystalline copper spheres. As a result of the applied deformation a void is generated at the center of the sphere. We analyze the formation of the void with respect to the type and strength of the shock applied. We correlate the size of the void with the peak stresses, the size of the original system, and compare to known scaling relations and with experiments. This work was carried out under the auspices of the US Department of Energy by Lawrence Livermore National Laboratory under contract W-7405-Eng-48.

**10:15 AM Break**

**10:30 AM**
**Heterogeneous Nucleation of Shock-Induced Plasticity and Phase Transformations**: *Timothy C. Germann*[1]; Brad Lee Holian[2];

Kai Kadau[3]; Peter S. Lomdahl[3]; [1]Los Alamos National Laboratory, X-7, MS D413, Los Alamos, NM 87545 USA; [2]Los Alamos National Laboratory, T-12, MS B268, Los Alamos, NM 87545 USA; [3]Los Alamos National Laboratory, T-11, MS B262, Los Alamos, NM 87545 USA

Large-scale ($10^6$ to $10^9$-atom) molecular dynamics simulations have been used to study plastic deformation and polymorphic phase transformations under shock loading. In addition to the homogeneous perfect crystals typically studied using smaller-scale simulations, larger samples enable the introduction of specific extended defects, or even nanocrystalline samples. Such heterogeneous nucleation sites are found to substantially lower the Hugoniot elastic limit (as compared with perfect crystals), as well as the phase transformation or detonation threshold pressure for polymorphic and energetic materials, respectively. Three prototypical systems will be discussed: (1) fcc metals, represented either by a generic Lennard-Jones pair potential or by an embedded atom method (EAM) potential for Cu; (2) the bcc-to-hcp transformation of solid iron; and (3) model energetic materials, represented by the diatomic ìABî model bond-order potential.

**10:45 AM**

**Influence of Grain Size on the Dynamic Deformation and Shock-Loading Response of Metals and Alloys**: *George (Rusty) T. Gray*[1]; Shuh-Rong Chen[1]; Kenneth S. Vecchio[1]; [1]Los Alamos National Laboratory, MST-8, MS G755, Los Alamos, NM 87545 USA

Ron Armstrong has made seminal contributions to the fields of high-rate deformation, constitutive modeling, and grain size effects on metal plasticity. This talk will discuss experimental results illustrating the role of grain size on the dynamic mechanical behavior, substructure evolution, and constitutive modeling of titanium, Monel 400, and zirconium. Increasing grain size is shown to significantly decrease the dynamic flow strength of Zr, Ti, and Monel 400 while increasing work-hardening rates in Ti and Zr due to an increased incidence of deformation twinning. The influence of grain size on dynamic mechanical behavior is discussed in terms of defect generation and storage mechanisms. The incorporation of grain size effects into constitutive models and validation using Taylor cylinder impact testing is presented.

**11:00 AM**

**The Mechanical Properties of 304 Stainless Steel After Explosive Shock Prestraining**: *S. A. Maloy*[1]; G. T. Gray[1]; C. M. Cady[1]; R. W. Rutherford[1]; R. Hixson[1]; [1]Los Alamos National Laboratory, MST-8, MS-H809, Los Alamos, NM 87545 USA

The mechanical properties of 304 stainless steel have been investigated in compression and tension at room temperature before and after explosive shock prestraining to a pressure of 35-45 GPa and compared to results from compressive testing of the annealed microstructure at a strain rate of 10-3/s. The microstructure evolution due to ìTaylor-waveî shock prestraining has been investigated using optical metallography and transmission electron microscopy. Mechanical testing results after explosive shock prestraining displays a factor of two increase in yield stress and a large reduction in ductility in tension. Microstructural analyses reveal increased twinning after ìTaylor-waveî prestraining and very little production of deformation induced martensite. The results are compared to previous results on high strain rate testing of 304 stainless steel specimens.

**11:15 AM**

**Deformation Mechanisms at Ultrahigh Pressures and Strain Rates**: *James M. McNaney*[1]; Bruce A. Remington[1]; Steven M. Pollaine[1]; K. Thomas Lorenz[1]; [1]Lawrence Livermore National Laboratory, Chem. & Matls. Sci., L-370, 7000 East Ave., Livermore, CA 94550-9234 USA

The use of high-energy lasers to produce shock loading conditions in solid materials is a relatively recent development. Sophisticated 2-D hydrodynamics simulations are used to characterize the transmission of the pressure wave through the material. Experimental verification of the predictions of these calculations is generally limited to VISAR measurements of the back side of thin foils. This work examines the use of microstructure in laser shock-loaded and recovered samples to detect deformation mechanisms and validate predictions based on hydrodynamic simulations of the laser-based drive. In order to test the accuracy of the complex hydrodynamic simulations, direct laser illumination was used to singly and/or doubly shock samples of an aluminum alloy. The material was recovered and subsequently examined metallographically to determine the extent of the ablation crater and the location of melted and refrozen material. Regions of material having been melted and refrozen were observed to have a small grain size (< 2 μm) as compared to that of the bulk material (< 30-40 μm). More detailed examinations, using transmission electron microscopy and/or orientation imaging microscopy were used to determine the presence of coarse slip bands and/or shear bands. Comparisons to results from similar material loaded by a high explosive drive will be made. This work was performed under the auspices of the US Department of Energy by the University of California, Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

**11:30 AM**

**Laser Induced Shock Compression of Copper: Orientation and Pressure Decay Effects**: *Matthew S. Schneider*[1]; Marc A. Meyers[2]; Fabienne Gregori[4]; Bimal Kad[1]; Daniel H. Kalantar[3]; Bruce Remington[3]; [1]University of California-San Diego, Matl. Sci. & Eng., 9500 Gilman Dr., 0418, La Jolla, CA 92093 USA; [2]University of California-San Diego, Dept. of Mech. & Aeros. Eng., 9500 Gilman, 0411, La Jolla, CA 92093 USA; [3]Lawrence Livermore National Laboratory, Livermore, CA 94550 USA; [4]University of Paris 13, Villetaneuse France

Copper monocrystals with [001] and [134] orientations were subjected to ultra-short shock pulses (~10 ns duration) induced by a laser. The deformation structure was significantly dependent on the crystallographic orientation, and distance from laser-impacted surface. The threshold stress for twinning in the [001] was 45 GPa compared with 55 GPa for [134]. Dislocation densities were also different for the two orientations. These results are rationalized in terms of a constitutive description of the slip twinning transition. The higher work hardening rate of the [001] orientation is responsible for increasing the shear stress in the specimens at the imposed strains, to a higher level than in the [134] orientation; this higher stress predisposes the onset of twinning in this orientation assuming both mechanisms are competitive. The orientation dependence of the twinning stress is much lower and expressed by the Schmid factors.

**11:45 AM**

**Orientational Dependence of Shock-Induced Plasticity and Chemistry in Diamond**: *Sergey V. Zybin*[1]; Mark Elert[1]; Carter T. White[2]; [1]US Naval Academy, Chem. Dept., Annapolis, MD 21402-5026 USA; [2]Naval Research Laboratory, Code 6189, 4555 Overlook Ave. SW, Washington, DC 20375 USA

Molecular dynamics simulations employing an empirical bond order potential are used to study the orientational dependence of the elastic-plastic shock wave structure and shock-induced chemistry in diamond. The mechanism of shock-induced plasticity within this model is found to depend crucially on the direction of shock wave propagation. For <110> oriented shock waves at piston velocities Up < 4.0 km/s a twinning deformation develops along the <112> direction while in <111> oriented shock wave at Up < 5.5 km/s the twinning is accompanied by considerable shearing in the lateral <110> direction, which favors formation of $sp^2$ hybridized bonds. However, for higher shock velocities the situation is changed. In the <110> shock waves at piston velocities > 6.0 km/s shear deformation now develops in the transverse <110> direction favoring the formation of layered carbon structures with a considerable number of $sp^2$ bonds while shock waves in the <111> direction show formation of diamond micrograins separated by amorphous carbon inclusions.

## Friction Stir Welding and Processing II: Friction Stir Joining: Process Models

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

*Program Organizers:* Kumar V. Jata, Air Force Research Laboratory, Materials & Manufacturing Directorate, WPAFB, OH 45433 USA; Murray W. Mahoney, Rockwell Science Center, Thousand Oaks, CA 91360 USA; Thomas J. Lienert, University of South Carolina, Mechanical Engineering Department, Columbia, SC 29208 USA; Rajiv S. Mishra, University of Missouri-Rolla, Metallurgical Engineering, Rolla, MO 65409-0340 USA

Tuesday AM | Room: 7B
March 4, 2003 | Location: San Diego Convention Center

*Session Chair:* Kumar V. Jata, Air Force Research Laboratory, Matls. & Mfg. Direct., WPAFB, OH 45433 USA

**8:30 AM**

**Material Flow and Temperature Distribution During Friction Stir Welding of 7050 Aluminum Alloy**: *Blair London*[1]; Murray Mahoney[2]; [1]Cal Poly State University, Matls. Eng. Dept., San Luis Obispo, CA 93407 USA; [2]Rockwell Scientific Company, Dept. 202, 1049 Camino dos Rios, PO Box 1085, Thousand Oaks, CA 91358-0085 USA

We used Al-30 vol.% SiC markers machined into one of the faying surfaces of the weld butt joint to track material flow during FSW. Though detailed metallographic studies, we were able to document the flow of material at the centerline, advancing, and retreating sides of the welds at various depths within the plate. We found significant differences in how much the material is strained and distributed in the FSW process with location in the weld. The experimental results are compared with those predicted by our computational model. Other marker materials in friction stir welded metals other than aluminum will also be discussed. The temperatures in the weld zones were measured with small-diameter thermocouples at various distances from the FSW nugget. In our design of experiments, we investigated the effects of weld parameters, location (advancing-retreating sides), and depth within the plate on the temperatures reached in the welding process. These results are compared with our modelís predictions.

**8:55 AM**
**2-Dimensional CFD Modelling of Flow Round Profiled FSW Tooling**: *Paul Andrew Colegrove*[1]; Hugh R. Shercliff[1]; [1]The University of Cambridge, Dept. of Eng., Trumpington St., Cambridge CB2 1PZ UK

This paper describes the application of the Computational Fluid Dynamics (CFD) code, FLUENT, to modelling of the metal flow in FSW. The primary goal is to assist in the development of new tools for FSW, though the models also improve the understanding of the deformation and heat generation mechanisms in FSW, and their relationship to the final weld microstructure. Friction stir models to date have focussed on thermal field prediction, with some studies leading to prediction of microstructural evolution, properties and residual stress. A much greater modelling challenge is the prediction and validation of the 3D flow field round the tool. Recent flow models have given some indication of the metal flow for idealised or conventional threaded tools, and some authors have speculated on the likely cause of weld defects. This paper describes progress towards developing a quantitative method of comparing the flow round different practical tool shapes. 2-D flow models have been used to compare four different tool profiles, and to examine the effect of changing rotation and welding speed on the process. To enable this comparison a novel ìslipî model was developed, in which the interface conditions were governed by the local shear stresses. This revealed significant differences in behaviour compared to the common assumption of sticking. The 2D model has demonstrated the viability of the approach for investigating the flow round practical tool shapes, and gives confidence that developing the more computer-intensive 3D models will be justified. The model also gives a first order visualisation of the flow round the central region of the probe in thick welds (i.e. well away from the influence of the shoulder or the probe base).

**9:20 AM**
**Tool Wear and Shape Optimization in the Friction-Stir Welding of Aluminum Metal-Matrix Composites**: *R. A. Prado*[1]; L. E. Murr[1]; D. J. Shindo[1]; A. R. Rivera[1]; J. C. McClure[1]; [1]University of Texas at El Paso, Dept. of Metallurgl. & Matls. Eng., 500 W. University Ave., El Paso, TX 79968 USA

In the friction-stir welding (FSW) of most aluminum alloys there is no perceptible wear of the pin tool even after traversing tens of meters of material. In the FSW of aluminum metal-matrix composites (MMCís) such as Al 6061 + 20% $Al_2O_3$ and Al-A339 + 20% SiC, tool wear has been shown to depend upon rotation and traverse speeds initially; with optimum wear occurring at 1000 rpm. However, as the traverse or actual weld speed is increased (from 1 mm/s to 9 mm/s) tool wear and tool wear rate decline. At 6 mm/s and 9 mm/s weld speeds (and constant rotation speed of 1000 rpm) the MMC FSW wear produces optimized tool shapes after sufficient traverse distances. Tool wear effectively ceases when these optimized shapes are achieved. Consequently, these shapes may provide a basis for designing optimized tools for other FSW systems as well.

**9:45 AM**
**Thermal and Microstructure Modelling in Thick Plate 7075 Friction Stir Welds**: Takehiro Hyoe[1]; *Paul Andrew Colegrove*[1]; Hugh R. Shercliff[1]; [1]The University of Cambridge, Dept. of Eng., Trumpington St., Cambridge CB2 1PZ UK

This paper investigates the evolution of precipitation hardening in thick plate friction stir welded aluminium alloy 7075-T7351. As part of a study into metal flow in FSW, thermal histories were produced as a function of position in the weld cross-section using the numerical fluid dynamics code, FLUENT. These were validated by thermocouple observation, and enabled detailed temperature prediction for the different regions in the weld, such as the nugget, thermo- mechanically affected zone (TMAZ) and heat-affected zone (HAZ). Isothermal softening experiments were conducted to capture the temperature-dependent fall in strength, which is due to a combination of precipitate dissolution and coarsening. Subsequent natural ageing was used to determine the extent to which strength could be recovered after welding. The data were fitted to a dissolution model developed for welding of ternary Al-Zn-Mg alloys. In spite of the added complexity of the phases in Cu-bearing alloys such as 7075, the model provides a useful tool for predicting the extent of softening and re-ageing due to the thermal cycles seen in 7075 friction stir welds. The model is applied to predict: (a) the extent of softening ahead of the probe, to investigate whether full dissolution has occurred prior to deformation; (b) the hardness profile across the TMAZ and HAZ. A number of possible complications in the precipitation behaviour, which are not incorporated in the current model, are discussed. It is likely in 7075 that there is an interaction between the dislocation structures and precipitation in the weld nugget and the TMAZ. This may lead to accelerated coarse precipitation (due to the alloyís quench sensitivity) during cooling of the weld, with a consequent decline in properties.

**10:10 AM Break**

**10:20 AM**
**Advances in Laser Assisted Friction Stir Welding**: *G. Kohn*[1]; Y. Shneor[1]; A. Munitz[2]; [1]Rotem Industries, Ltd., Temed Industl. Park, PO Box 9046, Beer-Sheva 84190 Israel; [2]Nuclear Research Center, PO Box 9001, Beer-Sheva 84190 Israel

Among the drawbacks of friction stir welding (FSW) is the need to use powerful fixtures to clamp the workpiece to the welding table, the high force needed to move the welding tool forwards and the relative high wear rate of the welding tool. To overcome these drawbacks a new laser assisted friction stir welding (LAFSW) system has been developed. The system is a combination of a conventional machining center and a Nd: YAG laser-system that are used together during the welding process. Laser power is used to pre-heat a volume of the workpiece ahead of the probe. The workpiece is then joined in the same way as in the conventional FSW process. The high temperature ahead of the rotating tool softens the workpiece and enables joining it without the need of strong clamping fixtures, reduces markedly the force needed to move the welding tool forwards and hence reduces its wear. This paper describes results that have been accumulated since the publication of the first paper. Comparison between the forces needed in FSW and LAFSW are presented for various geometries and materials and possible application of LAFSW in the aviation industry is suggested.

**10:45 AM**
**A New Coupled Heat Transfer Model for Friction Stir Welding**: *Mingde Song*[1]; Rado Kovacevic[1]; [1]Southern Methodist University, Dept. of Mechl. Eng., Rsrch. Ctr. of Adv. Mfg., 1500 International Pkwy., Ste. 100, Richardson, TX 75081 USA

In this paper, a new heat transfer model is established for modeling the three-dimensional transient heat-transfer in friction stir welding (FSW). The heat transfer between the tool and the workpiece are coupled at the interface. The heat flux input from the tool shoulder is calculated by the friction work; the plastic deformation heat near the pin is also modeled. The material latent heat is included in the model. An explicit central differential scheme is employed in solving the control equations. The calculation results are compared with the FSW experimental results, the two results are in good agreement. The welds at different welding control conditions are discussed.

**11:10 AM**
**Thermomechanical Processes in Friction Stir Welding**: *J. A. Schneider*[1]; A. C. Nunes[2]; [1]Mississippi State University, Dept. of Mechl. Eng., PO Box ME, 210 Carpenter Eng. Bldg., Mississippi State, MS 39762 USA; [2]NASA-MSFC, ED 33, Matls. Process & Mfg. Dept., Huntsville, AL 35812 USA

In friction stir welding (FSW), a rotating pin-tool stirs the edges of a weld seam together. The flow trajectories around the tool are illustrated by a thin (0.0025 in. diameter) tungsten wire marker and explained by a decomposition of the flow field into simpler elements. Two kinds of trajectories, each subjecting the weld metal to a distinct thermomechanical process and imparting a distinct microstructure, can be differentiated. Microstructures observed in a FSW cross-section in an aluminum 2195 alloy are related to their respective strain-temperature histories along their respective flow trajectories.

**11:35 AM**
**Modeling Friction Stir Welding Using an Inverse Problem Approach**: Sam G. Lambrakos[1]; *Richard W. Fonda*[1]; [1]Naval Research Laboratory, Matls. Sci. & Tech. Div., Code 6324, 4555 Overlook Ave. SW, Washington, DC 20375 USA

In contrast to the direct problem approach, which employs assumed values of material properties in coupled equations of energy, momentum, and mass transport to calculate the temperature histories occurring during welding processes, the inverse problem approach uses information about the actual temperature(s) achieved during welding to constrain calculations of the weld thermal field. This talk will discuss the application of this inverse problem approach to friction stir welding and its relationship to the direct problem approach. Finally, the model predictions will be compared to experimental data from thermocouple measurements, thermal simulations of the various regions of the friction stir welds, microhardness measurements, and microstructural characterizations in actual friction stir welds.

## General Abstracts: Smelting, Melting, and Effluent Control

*Sponsored by:* TMS
*Program Organizers:* TMS, Warrendale, PA 15086 USA; Eric M. Taleff, University of Texas, Mechanical Engineering Department, Austin, TX 78712-1063 USA

Tuesday AM — Room: 5A
March 4, 2003 — Location: San Diego Convention Center

*Session Chairs:* Robert L. Stephens, TeckCominco Metals Ltd., Trail, British Columbia V1R 4L8 Canada; Adrian Deneys, Praxair Inc., Tarrytown, NY 10591-6717 USA

**8:30 AM**
**Improved Maintenance Techniques for INCOís Two Flash Smelting Furnaces**: *Randy E. Lawson*[1]; Darryl D. Cooke[2]; [1]INCO, Ltd., Smelter Maintenance, Smelter Offices, Copper Cliff, Ontario P0M 1N0 Canada; [2]INCO, Ltd., Smelter Techl. Services, Copper Cliff, Ontario P0M 1N0 Canada

INCOís Copper Cliff Smelter houses two Flash Smelting Furnaces to process 100% of the copper-nickel concentrate produced from the Sudbury area mines. On-line time of these furnaces is key to maintaining throughput to the downstream processes. Increased furnace throughput and variations in slag temperature have resulted in accelerated wear of the furnace refractory. In order to minimize the effect of furnace downtime on production, an accelerated cool-down/repair/heat-up schedule was fabricated to fit within the schedule for repairs required to INCOís oxygen plant. The engineering of a unique system for supporting the furnace sidewalls allowed repairs to be completed on the high wear areas of the furnace including the matte tapholes. This paper also discusses the various techniques used for the furnace roof repairs, tie-ins to existing brickwork, co-ordination of mechanical and refractory contractors, replacement of a leaking uptake transition block and the achievements in the cool-down and heat-up schedules.

**8:50 AM**
**Observations on Blister Copper Spitting**: *Melissa L. Trapani*[1]; Ross K. Andrews[1]; Dennis Montgomerie[2]; Andrew K. Kyllo[1]; [1]The University of Melbourne, G. K. Williams Ctr. for Extractive Metall., Dept. of Cheml. Eng., Melbourne, Victoria 3010 Australia; [2]WMC Olympic Dam, PO Box 150, Roxby Downs, S. Australia 5725 Australia

ìBlister spittingî is a flow irregularity where the molten blister copper stream - or part thereof - sprays from the taphole exit rather than following a regular flow profile to the collection box. As well as being a general ìhousekeepingî issue, the unpredictable nature of the flow is a threat to operator safety. Also, the aggressive flow pattern may contribute to the mechanical wear of taphole refractory, compromising the integrity of the taphole. This paper brings together a collection of first-hand observations and reports from process personnel, and suggests some theories as to the causes of blister spitting.

**9:10 AM**
**Instrumentation of a Production Taphole**: *Melissa L. Trapani*[1]; Ross K. Andrews[1]; Dennis Montgomerie[2]; Andrew K. Kyllo[1]; Neil B. Gray[1]; [1]The University of Melbourne, G. K. Williams Ctr. for Extractive Metall., Dept. of Cheml. Eng., Melbourne, Victoria 3010 Australia; [2]WMC Olympic Dam, PO Box 150, Roxby Downs, S. Australia 5725 Australia

Many smelters have sought to improve their tapping systems, embarking on taphole development programs, which consist of a series of incremental modifications to an original taphole design. Modifying tapholes without sufficiently understanding them has led to the installation of hazardous tapholes, and in some cases dangerous and costly events have occurred. An improved taphole design methodology, developed specifically to avoid this scenario, is currently being applied to a production taphole. This paper provides: a discussion of the major challenges that come with the instrumentation of an industrial taphole, results from the plant trial, and the details of how these results are facilitating an improved taphole design.

**9:30 AM Cancelled**
**Improved Plugging Technology for Water Jackets in FS Furnaces**: *Pekka A. Taskinen*[1]; Veikko Polvi[1]; Tuija K. Suortti[1]; Ilkka V. Kojo[2]; Pekka Set‰l‰[3]; Pasi Ranne[4]; [1]Outokumpu Research, PO Box 60, Pori FIN-28101 Finland; [2]Outokumpu Technology, PO Box 862, Espoo FIN-02201 Finland; [3]Outokumpu Harjavalta Metals, Teollisuuskatu 1, Harjavalta FIN-29200 Finland; [4]Outokumpu Poricopper, Kuparitie, Pori FIN-28101 Finland

**9:50 AM**
**Non-Destructive Inverse Determination of Refractory Wall Material Wear Configurations in Melting Funaces**: *George S. Dulikravich*[1]; Thomas J. Martin[2]; [1]University of Texas at Arlington, Mech. & Aeros. Eng. Dept., Multidisciplinary Analy., Inverse Design & Optimization (MAIDO) Prog., UTA Box 19018, Arlington, TX 76019 USA; [2]Pratt & Whitney Engine Company, Turbine Discipline Eng. & Optimization Grp., 400 Main St., MS 165-16, E. Hartford, CT 06108 USA

From the existing thermocouples measurements on the outer surface of the hearth section of the furnace, it is possible to obtain both temperature and heat flux distribution on that surface. This provides for the over-specified thermal boundary conditions on this surface that is essential for our inverse algorithm, which can determine the corresponding temperature distribution on the guessed shape of the refractory/melt interface. If we insist that the wall refractory wear surface is at the melt solidus temperature, then only one possible wear surface configuration will have such isothermal condition. The correct shape of the wear surface is determined iteratively with our inverse shape determination algorithm that is based on an elastic membrane concept and Fourier series formulation. This inverse approach to inner wall shape determination is considerably faster than if utilizing an optimization algorithm thus providing for a real-time monitoring tool of wear surface configuration.

**10:10 AM Break**

**10:20 AM**
**Environmental Management of Selenium: Case Studies**: *Karen A. Hagelstein*[1]; [1]Times, Ltd., 1604 Leopard St., Sheridan, WY 82801 USA

This presentation will provide case studies in the environmental management of selenium from the aluminum, recycling, and mining industries. Selenium-containing waste streams, sources, and applicable USA regulations will be discussed. The toxicological and bioaccumulative properties of selenium will be outlined with respect to risk assessments and site specific criteria. Case studies will focus on monitoring, treatment, transport, and disposal practices in managing selenium wastes and emissions from primary and secondary aluminum operations. The sources of selenium such as dross, scrap, aluminum, and steel alloys containing manganese/selenium will be addressed. Secondary aluminum processing solid waste, such as baghouse dust, are subject to additional regulatory requirements if classified as hazardous by the toxicity characteristic leaching procedure (USEPA TCLP). Hazardous air pollutants (HAPs), including particulates and potentially selenium emissions, will be assessed with respect to operational variables, processed materials, treatment/control technologies, and health-based standards.

**10:40 AM**
**Nano-Filtration of Contaminated Solutions Using Avian Keratin Protein**: *Manoranjan Misra*[1]; *Piyush Kar*[1]; Ashok Raichur[2]; Carlo Licata[3]; Gautam Priyadarshan[1]; [1]University of Nevada-Reno, Mackay Sch. of Mines, Metall. & Matls. Eng., MS 388, Reno, NV 89557 USA; [2]Indian Institute of Science, Bangalore, Dept. of Metallurgl. Eng., Bangalore India; [3]MaXim Biosystems, 1015 N. Lake Ave., Ste. 313, Pasadena, CA 91104 USA

Avian Keratin Fiber is a form of animal fibrous protein and is derived from feathers of birds such as chicken and turkey and has been projected here as an ideal materials for biosorption and removal of metals from solutions. It is hydrophobic, stable over a wide pH range, and has a high surface area. It is an abundant bioresource and a cheap alternative to conventional adsorbents like activated carbon and ion-exchange resins. This material is primarily b-keratin and is nearly 100% protein in its constitution. The keratin protein fiber is an intricate network of protein fibers that are high in surface area and it consists of nano-sized pores. The nano-structure and the functional groups render the keratin fiber as an excellent nano-filter. The heavy metals that could be effectively removed included lead, copper, cadmium, zinc, chromium, iron, and mercury and precious metals like gold, platinum and palladium from process and drinking water to meet USEPA drinking water standards.

**11:00 AM**

**Efficient Treatment of Complex Wastewaters at Umicore Precious Metals Using Biotechnology**: Merijn Picavet[1]; Henk Dijkman[1]; *Johannes Boonstra*[1]; Klaas de Hoop[1]; Bert Daamen[1]; Wouter Ghyoot[2]; [1]Paques B.V., PO Box 52, Balk NL-8560AB Netherlands; [2]Umicore, Kasteelstraat 7, Olen B-2250 Belgium

Paques and Umicore have demonstrated the feasibility of biological treatment of the highly complex Hoboken wastewaters in a 1 m3/h pilot plant at Umicore Precious Metals, Hoboken, Belgium. The process consisted of the following main steps: 1. Arsenic precipitation with biogenic H2S as As2S3. 2. Biotechnological removal of nitrate combined with precipitation of dissolved metals as sulphides (MeS). 3. Biotechnological sulphate removal from the pretreated and denitrified waters using hydrogen as reductant. The sulphide produced was used for metals precipitation in steps 1 and 2. Excess sulfide was biologically oxidised and separated as solid elemental sulphur. Arsenic sulphide produced was easily separated using a tilted plate settler. Metals such as mercury, thallium, copper, zinc, lead, nickel were also removed to below discharge demands. Sulphate and nitrate were removed to low concentrations (<300 mg/l and < 5 mg/l respectively). Selenate was biologically reduced to elemental selenium to concentrations <0.2 mg/l.

**11:20 AM**

**Microwave Heating Characteristics of Pyrite and Microwave Assisted Coal Desulphurization**: *Tuncay Uslu*[1]; ‹mit Atalay[1]; [1]Middle East Technical University, Mining Eng. Dept., Ankara 06531 Turkey

In this study, microwave heating characteristics of pyrite mineral and desulphurization of coal by using magnetic separation following the microwave heating were investigated. Different size of pyrite samples were heated in microwave oven and heating characteristics were determined. It was observed that heating rates and maximum attained temperatures increased with increased microwave power level, heating time and reducing particle size. Microwave heated pyrite samples were subjected to magnetic separation and 98% of the pyrite was removed as magnetic product. Coal desulphurization by microwave heating followed by magnetic separation was also studied. Total and pyritic sulphur of coal sample were reduced by 32.82% and 37.46% respectively. With the addition of 7.5% magnetite into coal which is an excellent microwave absorber, the heating characteristics of coal sample was improved and total sulphur and pyritic sulphur content of coal sample were reduced 52.05% and 58.20% respectively by magnetic separation following the microwave heating.

## Global Development of Copper and Gold Deposits - I

*Sponsored by:* Extraction & Processing Division, EPD-Process Mineralogy Committee, EPD-Precious Metals Committee
*Program Organizers:* Tzong T. Chen, CANMET, Ottawa, Ontario K1A 0G1 Canada; Corby G. Anderson, Montana Tech of the University of Montana, Center for Advanced Mineral & Metallurgical Processing, Butte, MT 59701-8997 USA; Steven L. Chryssoulis, Amtel, London, Ontario N6G 4X8 Canada

Tuesday AM — Room: 1B
March 4, 2003 — Location: San Diego Convention Center

*Session Chairs:* Corby G. Anderson, Montana Tech of the University of Montana, Ctr. for Adv. Minl. & Metallurgl. Procg., Butte, MT 59701-8997 USA; T. T. Chen, CANMET, Ottawa, Ontario K1A 0G1 Canada

**8:30 AM**

**Remediating an Integrated Copper Complex-Problems in the Present and Lessons for the Future**: *Sandra M. Stash*[1]; Robert Ray Beebe[2]; Raymond E. Krauss[3]; [1]ARCO Environmental Remediation, 306 E. Park Ave., Anaconda, MT 59711 USA; [2]PO Box 4135, Butte, MT 59702-4135 USA; [3]6969 St. Helena Rd., Santa Rosa, CA 95404 USA

An integrated copper complex includes mining, milling and smelting facilities which are usually at or near a common site, and sized to complement one another in capacity. There may also be an electrolytic refinery serving the complex, but not always totally dedicated to its production. Mines and mills without co-owned smelters are not usually considered integrated. The first marketable product of an integrated complex is blister, or in some cases electrolytically refined copper. The nature of integrated operation brings together all of the environmental problems associated with copper production, but currently operating and newly planned facilities are required to anticipate these problems and meet stringent regulations. Older complexes, however, may have legacies of 50 or more years of operation unencumbered by environmental strictures: nevertheless, they must be remediated. Using examples from closures and remediations of the Anaconda/ARCO facilities in Montana, the authors review some of the problems encountered over more than a decade, and the means for their solutions, bearing in mind that not all of the problems and solutions were technical. Based on real-world experience, some potential pitfalls and lessons for the future are identified.

**9:00 AM**

**Behaviour of Gold During the Electrorefining of Copper**: *T. T. Chen*[1]; J. E. Dutrizac[1]; [1]CANMET, 555 Booth St., Ottawa, Ontario K1A 0G1 Canada

Copper sulphide ores and secondary materials contain trace amounts of Au. After smelting, the Au is collected in the copper anodes. In the copper anodes, the gold occurs in solid solution in the copper crystals. During electrorefining, the copper dissolves and the associated gold is released. Most of the gold reports as tiny metallic Au particles in the anode slimes. The Au shows a strong affinity for the selenide phase, and some of the metallic Au appears to have nucleated on the selenide particles. Some gold also appears to dissolve in the sulphate electrolyte, possibly because of the presence of chloride and thiourea, and subsequently to become incorporated as a minor constituent of a complex oxidate phase. Gold also is present both in solid solution in the selenide phase and as a Ag-Au-Cu selenide phase. Decopperizing of the anode slimes in an autoclave concentrates the gold as metallic Au, a Ag-Au selenide phase (Ag3AuSe2) and a Ag-AuSe-Te rich phase; the Ag-Au selenide phase appears to form during decopperizing. Also, the gold seems to be enriched in the original Ag selenide phase.

**9:30 AM**

**The Industrial Nitrogen Species Catalyzed Hydrometallurgical Recovery of Copper and Precious Metals from Chalcopyrite**: *Corby G. Anderson*[1]; [1]Montana Tech, Ctr. for Adv. Minl. & Metallurgl. Procg., 1300 W. Park St., Butte, MT 59701-8997 USA

Hydrometallurgical pressure oxidation of copper ores and concentrates is currently an active area of technological development. Of these, an overlooked but, ironically the first industrially proven methodology, utilized nitrogen species catalyzation in the oxidizing pressure leach system to produce copper via SX/EW. In this paper, the history of the system and its application to copper concentrates and ores will be outlined. In particular, the methodology for effective recovery of precious metals from chalcopyrite concentrates will be discussed. Finally, the perceived economics of chalcopyrite concentrate treatment with this unique industrially proven process will be delineated.

**10:00 AM**

**On the Floatability of Gold Grains**: *Stephen Chryssoulis*[1]; Stamen Dimov[1]; Daniela Venter[1]; [1]AMTEL, 100 Collip Cir., London, Ontario N6G 4X8 Canada

Accepted wisdom is that gold is naturally floatable in industrial systems, due to the adsorption of hydrocarbons which render hydrophobicity to gold grain surfaces. Such hydrophobicity is usually enhanced by the addition of flotation collectors such as xanthates, mono- and dithiophosphates and mercaptobenzothiolates. The mechanism invoked in enhancing the hydrophobicity of gold is similar to that of pyrite, whereby collector ions are oxidized at the gold surfaces to form the neutral dimers. The non-polar dimers are oily substances. Impurities in the gold (usually Ag and Cu) have been thought to form hydrophilic surface phases. Microbeam surface analysis of floated and rejected free gold grains from a number of commercial plants and pilot plant testwork has shown silver (the most common impurity in gold) and sulphur invariably in greater concentration on floated gold grains, implying that they assisted gold flotation. Further, collector loading measurements on individual gold grains from concentrates of sequential rougher flotation testwork revealed first progressively lower concentrations of the collector monomer on gold from each follow-up concentrate and secondly a direct proportionality between the surface concentration of silver and the collector monomer. Based on the available data there is no doubt that silver activitates and that collector monomers play a significant, previously not recognized, role in gold flotation.

**10:30 AM**
**Microwave-Assisted Chalcocite Leaching in $CuCl_2$-NaCl Media Under Oxygen Pressure**: *Jiann-Yang Hwang*[1]; Shangzhao Shi[1]; Xiaodi Huang[1]; [1]Michigan Technological University, Inst. of Matls. Procg., 309 Minerals & Matls. Bldg., 1400 Townsend Dr., Houghton, MI 49931-1295 USA

A study on microwave assisted chalcocite leaching was carried out with a microwave hydrothermal reactor. The leaching media is a mixed solution Of $CUC1_2$ and NaCl. The leaching temperature, oxygen pressure, stirring speed, quantities of the minerals per unit solution volume as well as the initial concentration of cupric and chloride ions were investigated as the process parameters. The results were discussed and compared with that using conventional leaching method.

## Hot Deformation of Aluminum Alloys: Constitutive Analysis, Modeling and Simulation

*Sponsored by:* Materials Processing and Manufacturing Division, MPMD-Shaping and Forming Committee
*Program Organizers:* Zhe Jin, Alcoa Technical Center, Thermomechanical Processing and Alloy Development, Alcoa Center, PA 15069 USA; Armand J. Beaudoin, University of Illinois at Urbana-Champaign, Department of Mechanical and Industrial Engineering, Urbana, IL 61801 USA; Thomas R. Bieler, Michigan State University, Department of Chemical Engineering and Materials Science, East Lansing, MI 48824-1226 USA; Balasubramaniam Radhakrishnan, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6359 USA

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|---|---|
| Tuesday AM | Room: 6E |
| March 4, 2003 | Location: San Diego Convention Center |

*Session Chairs:* Julian H. Driver, Ecole des Mines de St Etienne, SMS, St. Etienne 42023 France; Mary A. Wells, University of British Columbia, Dept. of Metals & Matls. Eng., Vancouver, BC V6T 1Z4 Canada; Rustam Kaibyshev, Institute for Metals Superplasticity Problems, Ufa 450001 Russia

**8:30 AM Invited**
**Atomistic Modeling of Hot Deformation of Disordered Al-Ni Alloys**: *S. G. Srinivasan*[1]; M. I. Baskes[1]; [1]Los Alamos National Laboratory, MST-8, MS G755, Los Alamos, NM 87545 USA

An understanding of hot deformation in Al-Ni alloys can provide insight for many thermomechanical-processing technologies. Hot deformation processes produce complex interactions between grainboundaries and dislocations, which eventually lead to unusual defect microstructures with practical implications. We systematically study the interaction of a lattice edge dislocation with a grainboundary in disordered Al-Ni alloys, with up to 10% Ni, as a function of shear. Bicrystals with a dislocation in one of the grains were crafted with various symmetric and asymmetric tilt grainboundaries. Molecular dynamics simulations using a reliable embedded atom method potential were performed on these bicrystals at close to (2/3)rd the melting temperature. Local grain and defect structures were examined using a common neighbor analysis. This information coupled with an intimate knowledge of stress-strain behavior will provide insight into deformation processes at high temperatures.

**8:55 AM Invited**
**Damage Evolution in Hot Deformation: Nano-Micro-Mesoscale Growth**: *Amit K. Ghosh*[1]; [1]University of Michigan, Matls. Sci. & Eng., 2102 H. H. Dow Bldg., 2300 Hayward St., Ann Arbor, MI 48109-2136 USA

Engineering metals and alloys exhibit formation of voids during large plastic deformation at elevated temperature, a matter of concern in metal forming processes. Typically such void formation occurs at and near grain boundaries, since at elevated temperature grain boundary sliding, albeit small at times, provide an accommodating mechanism for deformation. Thermomechanical processing and casting often leave fine scale damage in materials, particularly at hard second phase particles and grain boundaries. These damages can grow during subsequent deformation primarily by a strain-controlled process. It is often believed that recrystallization and homogenization treatments can heal damage and rid material of all preexisting damage. Recent findings suggest that this notion is only approximately true. ìApparently healedî voids may only represent a weak interface, which may contain nanometer scale voids. As these nanovoids provide free surfaces, they experience deviatoric stresses during deformation and can grow by dislocation accumulation at their tips. Gradual and statistical opening of these nanovoids give rise to a ìcontinuous nucleationî phenomenon. In other cases, nucleation truly requires a sufficiently high local stress generated in the vicinity of phase boundaries that are incompatible. In this talk, growth of such voids and the role of healing processes on subsequent damage evolution will be discussed.

**9:20 AM Invited**
**Application of Mesoscale Finite Element Simulations to Study the Evolution of Cube Texture During Hot Deformation of Aluminum**: *Gorti B. Sarma*[1]; B. Radhakrishnan[1]; Thomas Zacharia[2]; [1]Oak Ridge National Laboratory, Compu. Sci. & Math. Div., PO Box 2008, MS-6359, Oak Ridge, TN 37831-6359 USA; [2]Oak Ridge National Laboratory, Compg. & Computatl. Sci. Direct., PO Box 2008, MS-6232, Oak Ridge, TN 37831-6232 USA

The origin and development of cube ({001}<100>) texture during hot deformation and subsequent recrystallization of aluminum alloys remains a topic of considerable interest in materials research. The application of finite element modeling at the mesoscale to study the hot deformation of microstructures containing cube oriented grains distributed among grains with S ({123}<634>) and copper ({112}<111>) orientations is described. Discretization of each grain with a large number of elements enables the model to capture the heterogeneous deformation of individual grains. The constitutive response of the material is modeled using crystal plasticity, thereby enabling the prediction of texture evolution in the microstructure. The deformation at elevated temperatures has been modeled by including slip on the non-octahedral {110}<110> systems, in addition to the usual {111}<110> systems. Microstructures with different grain sizes have been deformed in plane strain compression. The effects of the local environment, grai n size and plastic strain on the stability of the cube texture during hot deformation are examined. Research sponsored by the Office of Basic Energy Sciences, US Department of Energy, under contract DE-AC05-00OR22725 with UT-Battelle, LLC.

**9:45 AM**
**Dynamic Response of AA7075 Aluminum Alloy as a Function of Temperature**: *Zhe Jin*[1]; William A. Cassada[1]; Carl Cady[2]; George (Rusty) T. Gray[2]; [1]Alcoa Technical Center, Alcoa Ctr., PA 15069 USA; [2]Los Alamos National Laboratory, Los Alamos, NM 87545 USA

The dynamic behavior of a commercial 7075 aluminum alloy was studied as a function of temperature. The dynamic stress-strain response of the 7075 aluminum alloy at 2100 s-1 can be characterized into two temperature regimes: (1) athermal hardening dominates at temperatures £200∞C and (2) thermally activated recovery dominates at temperatures ≥300∞C. The largest drop in the dynamic flow stress with temperature occurs at temperatures between 200∞C and 300∞C and the smallest at temperatures above 300∞C. Guiner-Preston (GP) zones and h precipitates are the major strengthening components for the dynamic loading of the 7075 aluminum alloy. Strain instability and adiabatic heating appears to have a significant impact on the dynamic response of the 7075 aluminum alloy, particularly at the lower test temperatures.

**10:05 AM**
**Localized Deformation in Hot Working of AA 7XXX Alloys**: *Henry A. Padilla*[1]; Blythe E. Gore[2]; Armand J. Beaudoin[1]; Jonathan A. Dantzig[1]; Ian M. Robertson[2]; Hasso Weiland[3]; [1]University of Illinois at Urbana-Champaign, Mechl. & Industl. Eng., 1206 W. Green St., MC-244, Urbana, IL 61801 USA; [2]University of Illinois at Urbana-Champaign, Matls. Sci. & Eng., 1304 W. Green St., MC-246, Urbana, IL 61801 USA; [3]Alcoa Technical Center, 100 Techl. Dr., Alcoa Ctr., PA 15069 USA

In hot working of 7xxx series aluminum alloys, the thermomechanical processing window is limited by problems such as hot shortness and by property requirements such as fatigue and fracture toughness. The mechanical response of AA 7050 and AA 7055 was first characterized using routine compression test procedures. A novel test procedure was then developed to study the onset of localization due to hot shortness. Compression samples were encased in a sheath of commercial purity aluminum. The test provides for a transition from homogeneous to non-uniform deformation, as dictated by mechanical integrity of the grain boundaries. There is a concomitant progression in the controlling mechanism for mechanical anisotropy from crystallographic texture to grain morphology. The results are interpreted through complementary studies of microstructure evolution.

**10:25 AM Invited**
**Mesoscale Simulation of Cube Texture Evolution Following Hot Deformation of Aluminum**: *Bala Radhakrishnan*[1]; Gorti Sarma[1]; [1]Oak Ridge National Laboratory, Compu. Sci. & Math. Div., Bldg. 6025, MS 6359, Oak Ridge, TN 37831-6359 USA

It is well known that cube bands that survive the hot deformation process serve as nuclei for subsequent cube texture evolution in aluminum during recrystallization. The interfacial area between cube and S orientations appears to be the key microstructural feature that controls cube nucleation. The paper presents simulations of cube texture evolution at the mesoscopic length-scale with emphasis on the influence of local microstructural environment on the growth of cube islands after hot deformation. Hot deformation substructures derived from crystal plasticity based modeling are used as input to a Monte Carlo based simulation of substructure evolution. The effect of neighboring orientations such as Copper and S on the growth of cube bands is investigated as a function of plastic strain and initial grain size. The simulation results are compared with the predictions of existing analytical models of texture evolution in polycrystalline aluminum. Research sponsored by the Office of Basic Energy sciences, US Department of Energy under contract DE-AC05-00OR22725 with UT-Batelle, LLC.

**10:50 AM**
**A Finite Element Model for Crystal Plasticity During Large Deformation and Comparison with Experimental Measurements**: Rajesh Prasanna[1]; Pankaj Trivedi[1]; *Ben Q. Li*[1]; David Field[1]; [1]Washington State University, Sch. of Mechl. & Matls. Eng., Pullman, WA 99164-2920 USA

A finite element-based macro/micro model is presented for crystal plasticity during large deformation of aluminum alloys. The model development is based on the updated Lagrangian formulation for large plastic deformation with the product decomposition of the deformation gradient tensor into elastic and plastic parts. This total formulation will ensure both the strong and weak objectivity for large plastic deformations. The macroscopic stress is linked to the microstructural behavior of crystals by tracking the motion of the active slip systems underlining the plastic deformation. Our model treatment entails a multi-surface-type stress update algorithm, which ensures the plastic deformation defined by each slip system to be on the yield surface. The numerical model is first applied to a single crystal system undergoing plastic deformation and then applied to a poly-crystal system involving a few grains. The numerical formulations and algorithm implementation are presented and numerical simulations are compared with experimental measurements.

**11:10 AM**
**Simulation of Extrudate Surface Formation by the Use of Finite Element Method**: *Xinjian Duan*[1]; Terry Sheppard[1]; Xavier Velay[1]; [1]Bournemouth University, Sch. of Design, Eng. & Compu., 12 Christchurch Rd., Bournemouth, BH1 3NA England

To have a better control in surface quality of the extruded products, it would be very helpful to know which part of the as-cast billet forms the extrudate surface. The limitations of the current experimental techniques have restricted the quantitative study on the formation of outer layer of the extrudate. In this paper, a commercial FEM code, FORGE2®, is adopted to study the material flow in both direct and indirect extrusion of aluminium alloys. The validity of the FEM simulation for the study of surface formation is first verified by comparing the simulated results with those experimental observations when a flat-faced nonlubricated die is used. Then, the FEM is used to study the influence of various forming parameters (such as punch temperature, billet/container temperature differential) and the die configuration on the formation of extrudate surface in both direct and indirect extrusion.

**11:30 AM**
**Parametric Studies of FSW Using a 2-D, Fluid Based Simulation**: *Anthony Peter Reynolds*[1]; Wei Tang[1]; Tianzhong Long[1]; [1]University of South Carolina, Dept. of Mechl. Eng., 300 Main St., Rm. A224, Columbia, SC 29208 USA

Accurate simulation of the FSW process will enable rapid development of the process in particular with regard to tool design. However, this type of simulation requires a 3-D, fully coupled thermo-mechanical, solid based model with associated high computational cost. In previous work, some of the authors have demonstrated that a 2-D model using a commercial fluid dynamics code and an appropriate user defined viscosity law can accurately capture many of the trends observed in FSW. The fully thermo-mechanically coupled simulations may be run in a few hours on a PC based system. The low computational cost for this model enables rapid assessment of the effects of various material properties and the criticality of inclusion or exclusion of some property details. In this paper, the effects of varying thermal diffusivity, viscosity, strain rate sensitivity etc. on the trends in x-axis forces, required torques, and locations and magnitudes of pressure minima and maxima are examined. The model trends are compared to experimental observations wherever possible.

**11:50 AM**
**Modeling of Friction Stir Joining as a Metalworking Process**: *William J. Arbegast*[1]; [1]South Dakota School of Mines and Technology, Adv. Matls. Procg. Ctr., 501 E. St. Joseph St., Rapid City, SD 57701 USA

A ìMechanistic FSW Modelî has been developed which describes the FSW process in terms of five conventional metal working zones: a) preheat, b) initial deformation, c) extrusion, d) forging, and e) post heat/cool down. A simple approach to flow modeling using mass balance considerations reveals a relationship between pin tool geometry, operating parameters, and flow stress of the materials being joined. Comparing flow to the extrusion of material around the pin tool provides for calculation of the width of the extrusion zone, strain rates, and x-direction forces. Coupled with empirically determined relationships between processing parameters, maximum temperature, heating and cooling rates, and, material constituitive properties from Gleeble data, an understanding of the conditions necessary to produce an ìoptimumî weld emerge. Examples of this analysis approach to FSW optimization for 7050 and 6061 aluminum with comparison to experimental observations are presented.

## Increasing Energy Efficiency in Aluminum

*Sponsored by:* Light Metals Division, LMD-Aluminum Committee
*Program Organizer:* Subodh K. Das, Secat, Inc., Coldstream Research Campus, Lexington, KY 40511 USA

Tuesday AM — Room: 5B
March 4, 2003 — Location: San Diego Convention Center

*Session Chairs:* Subodh K. Das, Secat Inc., Coldstream Rsrch. Campus, Lexington, KY 40511 USA; Sara Dillich, US Department of Energy, Office of Industl. Tech., Washington, DC 20585-0121 USA

**8:30 AM**
**Aluminum Research and Development**: *Thomas Robinson*[1]; [1]US Department of Energy, Aluminum Tech., Industl. Techs. Prog., Washington, DC USA

The Department of Energy - Industrial Technologies Program (DOE-OIT) is partnering with more than seventy organizations on over thirty research and development projects that reduce energy consumption and address research priorities identified in the Aluminum Industry Technology Roadmap. DOE-OIT will present an overview of its Aluminum R&D portfolio, covering technical progress, expected benefits, demonstration status, and market impacts. DOE-OITís focus is energy reduction and it uses technology roadmaps to ensure that its R&D programs address the industryís energy needs. DOE-OIT recently participated in the development of an Alumina Technology Roadmap and will publish a new Aluminum Industry Technology Roadmap by the end of 2002 that will reexamine the technology needs outlined in the 1997 Roadmap and identify new needs based on changes to the industry. DOE-OIT will also present how roadmaps influence R&D priorities.

**8:45 AM**
**Updating the Aluminum Industry Technology Roadmap**: *Richard Love*[1]; Mike Skillingberg[2]; Thomas Robinson[3]; Ross Brindle[4]; [1]Century Aluminum, Ravenswood, WV USA; [2]The Aluminum Association Inc., Tech., Washington, DC USA; [3]US Department of Energy, Aluminum Tech., Industl. Techs. Prog., Washington DC USA; [4]Energetics, Inc., Columbia, MD USA

In 1997, under the leadership of The Aluminum Association Inc. and the U.S. Department of Energy, the aluminum industry developed the Aluminum Industry Technology Roadmap, a comprehensive, long-term technology agenda for the entire industry. The Roadmap outlined quantitative performance targets, technical barriers, and research and development needed to achieve industry goals for increasing productivity, reducing costs, expanding markets, saving energy, improving worker health and safety, and minimizing environmental impact. Over the past five years, the Roadmap and its five companion ìsub-roadmapsî have stimulated over $100 million in cost-shared R&D projects with over 75 different organizations, including aluminum companies, suppliers, national laboratories, universities, and other research organizations. In November 2001, the aluminum industry published a new vision of its future. This vision, Aluminum Industry Vision: Sustainable Solutions for a Dynamic World outlines the new challenges that have emerged over the past five years and presents a bold vision of the industryís future, including a new set of industry goals. To ensure technology development remains aligned with the industryís vision, 50 representatives of aluminum companies, vendor companies, universities, national laboratories, and other researchers gathered in Pittsburgh, Pennsylvania in September 2002 to begin the process of updating the industryís Roadmap. At the workshop, participants identified technical barriers and R&D priorities in four areas: primary production; melting, solidification, and recycling; fabrication; and finished products. The Aluminum Associationís Technical Advisory Committee has taken the lead responsibility in preparing and implementing this newly revised Roadmap.

**9:15 AM**

**Energy Efficiency Improvement Opportunities in the Aluminum Industry**: *Arvind Thekdi*[1]; Sara Dillich[2]; [1]E3M, Inc., 15216 Gravenstein Way, N. Potomac, MD 20878 USA; [2]Department of Energy, Efficiency & Renewable Energy, 1000 Independence Ave., Washington, DC 20585-0121 USA

The United States is the largest single producer of primary aluminum. Total energy used by the aluminum industry (year 1995) in USA is approximately 700 trillion (10^12) Btu/year which represents approximately 2.5% of the total industrial energy use for the United States. It is one of the most energy intensive industry where energy cost represent approximately 30% of the total cost of production in USA. Although substantial improvements have been made in the energy consumption per unit of production by the industry during the last two decades, the industry can still do a better job to make further improvements. The aluminum industry plants use energy for primary metal production, primary and secondary aluminum melting and subsequent fabrication processes. The energy supplied to primary metal production is mostly in the form of electricity while the secondary aluminum melting and fabrication processes use fossil fuel (natural gas) for furnaces and electricity for rolling operations, compressors, fans and blowers, pumps, etc. Each of the energy using equipment offer an opportunity to improve their energy efficiency that can lead to substantial improvements in overall energy efficiency. This paper describes major areas of energy use and current status of energy use patterns for the primary and secondary aluminum industry and the available tools for evaluation of the current energy use and energy efficiency improvements. It outlines results of plant wide energy assessments carried out by the aluminum companies in cooperation with The Department of Energy. The paper highlights opportunities for efficiency improvement supplemented by examples of specific actions taken by the industry for energy efficiency improvement.

**9:45 AM Break**

**10:00 AM**

**Improving Energy Efficiency in Secondary Aluminum Melting**: *Paul E. King*[1]; Tianxiang Li[2]; Mohamed Hassan[2]; Kozo Saito[2]; Srinath Viswanathan[3]; Qingyou Han[3]; Shen-Lin Chang[4]; David Hoecke[5]; [1]US Department of Energy, Albany Rsrch. Ctr., 1450 Queen Ave. SW, Albany, OR 97321 USA; [2]University of Kentucky, Dept. of Mechl. Eng., Lexington, KY 40506 USA; [3]Oak Ridge National Laboratory, Metals & Ceram. Div., Bethel Valley Rd., Oak Ridge, TN 37831-6083 USA; [4]Argonne National Laboratory, Analysis, Simulation & Modlg., 9700 S. Cass Ave., Argonne, IL 60439-4815 USA; [5]Enercon Systems, Inc., 300 Huron St., Elyria, OH 44035 USA

The objectives of ìImproving Energy Efficiency in Aluminum Meltingî project is to develop technology or to indicate operational variations that will improve the energy efficiency in aluminum melting by 25%, reduce emissions of GHG and NOx, and increase overall productivity of the aluminum industry. Estimates show that the transfer of technologies developed during this project has the potential of saving $57 million dollars/year in natural gas fuel costs (~13 trillion Btu/year) when fully implemented by the year 2015. The project utilizes a multi-company, multi-laboratory consortium to study the efficiency of the aluminum industry today and to perform the necessary research to overcome the obstacles identified as holding the efficiency of the melting technologies below a pre-defined minimum. The research team consists of three national laboratories, Secat, Inc., UK-CAT, nine participating aluminum companies and 3 industrial partners representing combustion and metal pumping/stirring technologies. This group is exceptionally strong in the aluminum melting arena with several hundred years of experience in aluminum melting technologies. The research has been divided into 4 separate but intimately coupled parts which include a) computational modeling of the combustion space for each of the furnace types, b) measurement and analysis of current steady state melting practices utilized by the member companies, c) synthesis of the measurements and the combustion space modeling into a detailed furnace model and d) experimentation. Substantial effort has gone into each of these categories with some of the general results presented in this report.

**10:30 AM**

**Reduction of Oxidative Melt Loss**: *John N. Hryn*[1]; [1]Argonne National Laboratory, 9700 S. Cass Ave., Argonne, IL 60439 USA

This presentation will describe the efforts of a collaborative, multidisciplinary project involving Secat, Inc., seven of its member aluminum companies, the Center for Aluminum Technology at the University of Kentucky, Argonne National Laboratory, Oak Ridge National Laboratory, and Albany Research Center. The project, jointly funded by DOE/OIT Aluminum Industry of the Future program and Secat, Inc., aims to reduce melt loss during aluminum melting by 50%. To that end, the project objectives are to (1) develop an understanding of the key factors that contribute to the oxidation of molten aluminum, (2) determine the effects of major variables on the formation of dross during heating, melting, and holding of the melt at temperature, and (3) develop and evaluate technology that will reduce melt loss. Techniques used to investigate the in-situ oxidation of the molten metal surface included X-ray diffraction, X-ray fluorescence, and X-ray photoelectron spectroscopy. Microstructural analyses of industrial and lab-grown dross were also performed. Solid-state NMR was used to investigate spinel formation in dross. A small reverberatory furnace was constructed for melt trials.

**11:00 AM**

**Modeling and Optimization of Direct Chill Casting for Reducing Ingot Cracking**: *Srinath Viswanathan*[1]; Qingyou Han[1]; Adrian S. Sabau[1]; Lee Davis[2]; John A. Clark[3]; Kazunori Kuwana[4]; Mohamed I. Hassan[4]; John Hryn[5]; Greg Krumdick[5]; [1]Oak Ridge National Laboratory, Metals & Ceram., Bldg. 4508, MS 6083, Oak Ridge, TN 37831-6083 USA; [2]Wagstaff, Inc., 3910 N. Flora Rd., Spokane, WA 99216-1720 USA; [3]Albany Research Center, 1450 Queen Ave. SW, Albany, OR 97321 USA; [4]University of Kentucky, Mechl. Eng. Dept., 513 CRMS Bldg., Lexington, KY 40506-0108 USA; [5]Argonne National Laboratory, 9700 S. Cass Ave., Bldg. 362, Argonne, IL 60439-4815 USA

The goal of the project is to assist the aluminum industry to reduce the incidence of cracks from a current level of 5% down to 2%. This is important for improving product quality and consistency as well as saving resources and energy, since considerable amounts of cast metal could be saved by eliminating ingot cracking, by eliminating butt sawing. The project is a collaboration of industry, university, and national laboratory personnel through Secat, a consortium of aluminum companies. It will focus on the development of a detailed model of thermal conditions, solidification, microstructural evolution, and stress development during the initial transient in DC casting. In addition, it will develop criteria for the prediction of crack formation based on a fundamental understanding of the interaction of the as-cast microstructure, the local stress, and solidification conditions. The models developed in the project will be implemented in a commercial casting code so that they will be accessible to industry and be amenable to refinement in the future. This paper provides an overview of developments to date on experimental measurements of heat transfer at the ingot surface, inverse calculation of heat transfer coefficients, characterization of the solidification microstructure, computer models of the DC casting process for predicting the temperature and stress fields, and the determination of material properties in the mushy zone.

**11:30 AM**

**DOE/OIT PHAST Program Application in the Aluminum Industry**: *Frank L. Beichner*[1]; [1]Bloom Engineering Company, 5460 Horning Rd., Pittsburgh, PA 15236 USA

Increasing utility prices has placed an increased emphasis on reducing energy usage at many major industrial facilities. The U.S. Department of Energy (DOE) with cooperation from Industrial Heating Equipment Association (IHEA) and the major industries has developed the Process Heating Assessment and Survey Tool (PHAST) to assist in assessing and determining the major energy users for a facility, facilitating management in targeting where resources should be expended. This paper will discuss the results obtained by using the PHAST tool by Bloom Engineering Company at the Alcoa facility in Tennessee to provide an assessment of the plants energy usage. Particular emphasis will be placed on the usefulness of the information gathered and the assistance gained in determining both their overall plant efficiency and the equipment where emphasis for energy reduction should be concentrated. Also, the programs tools for assessing current designs against possible improvements will be shown.

**11:45 AM**
**Retrofitting Regenerative Burners on Aluminum Melting Furnaces that Utilize Salt Fluxing**: *Jens H. Hebestreit*[1]; *Marc D. Wolitz*[2]; [1]Bloom Engineering, Eng., Horning Rd. 5460, Pittsburgh, PA 15236-2822 USA; [2]Owens Corning Metal Systems, Eng., 1891 Reymet Rd., Richmond, VA 23237 USA

Rising fuel prices have placed an increased emphasis on reducing the cost to melt aluminum. Regenerative burner technology has been a fuel savings option for years in the aluminum industry, but maintenance, especially when using salt fluxing, has deterred many Casthouse managers from installing these systems. This paper will discuss a side well melting furnace retrofit from a cold air system to a regenerative system. The decision process detailing the conversion to regenerative rather than other technologies such as oxy/fuel is due to the production increases obtained and fuel savings achieved with the regenerative system. Also, the salt fluxing effect on media plugging and the steps taken to minimize this effect on production and maintenance will be addressed.

## International Symposium on Gamma Titanium Aluminides: Fatigue and Fracture

*Sponsored by:* Structural Materials Division, ASM International: Materials Science Critical Technology Sector, ASM/MSCTS-Materials & Processing, SMD-High Temperature Alloys Committee, SMD-Titanium Committee
*Program Organizers:* Young-Won Kim, UES, Inc., Materials & Processes Division, Dayton, OH 45432 USA; Helmut Clemens, GKSS, Institute of Materials Research, Geesthacht D-21502 Germany; Andrew H. Rosenberger, Air Force Research Laboratory, Materials & Manufacturing Directorate, Wright-Patterson AFB, OH 45433-7817 USA

Tuesday AM Room: 6F
March 4, 2003 Location: San Diego Convention Center

*Session Chairs:* Robert O. Ritchie, University of California, Matls. Sci. & Eng., Berkeley, CA 94720-1760 USA; Paul Bowen, University of Birmingham, Metall. & Matls., Birmingham B15 2TT UK

**8:30 AM Invited**
**The Influence of Microstructure on Crack Initiation & Early Growth in Gamma TiAl Alloys**: *Andrew H. Rosenberger*[1]; [1]Air Force Research Laboratory, Matls. & Mfg. Direct., AFRL/MLLMN, 2230 Tenth St., WPAFB, OH 45433-7817 USA

The incorporation of gamma titanium aluminide alloys as rotating components in gas turbine engines will require the application of a damage tolerant design philosophy. Since gamma alloys exhibit a steep crack growth rate curve and relatively low fracture toughness design methodology will likely require damage tolerance through an assurance that a crack at a defected location will not grow to failure. In this case the mechanisms of crack initiation and early growth are critical. This study examined the mechanisms of fatigue crack initiation in lamellar gamma TiAl alloys with various microstructural scales. Crack initiation was detected using a high-resolution direct current potential difference system capable of detecting small cracks (>300 mm) in a moderately large sample. The role of microstructure was found to play a dominant role in the cracking. Significant differences in crack initiation under cyclic and monotonic loading were realized.

**9:00 AM**
**Physics-Based Model to Predict the Fatigue Response of Gamma TiAl**: *Robert G. Tryon*[1]; Animesh Dey[1]; [1]VEXTEC, 116 Wilson Pike, Ste. 230, Brentwood, TN 37027 USA

A physics-based modeling technique incorporating Monte Carlo simulation is used to predict the statistical behavior of fatigue in fully lamellar gamma TiAl. The simulation relates the random nature of the microstructure to the fatigue response of smooth round bar specimens. Microstructural characteristics such as colony size, available slip systems and critical local shear stresses are considered. The results of the research effort showed that models addressing the microstructural mechanisms that govern fatigue damage accumulation could be combined with the concept of mesomechanics to properly account for the characteristic sizes and multiple phases of fatigue. The capability developed can be used to virtually test large numbers of specimens for which actual laboratory testing would be cost prohibitive.

**9:20 AM**
**Fatigue Properties of a Ti-48Al-2Cr-2Nb Alloy Produced by Casting and Powder Metallurgy**: *Gilbert HÈnaff*[1]; Anne-Lise Gloanec[1]; Marjolaine Grange[2]; Philippe Belaygue[3]; [1]ENSMA, LMPM, 1 Ave. Clement Ader, BP 40109, Futuroscope Chasseneuil 86961 France; [2]Snecma Moteurs, Matls. & Proc. Dept., Moissy Cramayel F-77550 France; [3]Turbomeca, Bordes F-64511 France

This paper deals with an on-going study on the fatigue properties of a quaternary Ti-48Al-2Cr-2Nb alloy produced by casting (nearly-fully lamellar microstructure) and by powder metallurgy (duplex microstructure with a high fraction of gamma grains). Low cycle fatigue tests at room temperature reveal a cyclic strain hardening of the cast material which is strongly dependent on the applied strain amplitude. In particular, a pronounced hardening was observed at high strain amplitude, associated with extensive twinning, although the stabilization of the stress amplitude at lower strain amplitude can lead to the formation of a classical vein-like structure. Such a pronounced hardening was not observed in the powder metallurgy alloy. Besides the near-threshold fatigue crack growth behavior is not strongly dependent on microstructure. In the high crack growth rate regime however, the cast alloy exhibits a superior resistance.

**9:40 AM Invited**
**Fracture of Lamellar TiAl: The Role of Lamellae Misorientation Across Colony Boundaries**: *Sharvan Kumar*[1]; Ping Wang[1]; Nitin Bhate[2]; Kwai S. Chan[3]; [1]Brown University, Div. of Eng., Box D, 182 Hope St., Providence, RI 02912 USA; [2]General Electric Global Research Center, Niskayuna, NY 12309 USA; [3]Southwest Research Institute, San Antonio, TX 78238 USA

Results of in-situ fracture experiments in the SEM of compact tension specimens of a binary TiAl alloy with a lamellar microstructure suggested that colony boundaries can provide crack growth resistance. However, the presence of sub-surface colonies in the specimen precluded unambiguous conclusions from being drawn concerning conditions under which such resistance could be expected. Furthermore, damage observed ahead of the advancing crack tip within a colony could also be influenced by the presence of sub-surface colonies. Therefore, a substantial investigation was undertaken to study crack growth in single-colony thick specimens that were however polycolony in the specimen plane. In such specimens, colony boundaries were characterized by the lamellar misorientation across them (a kink angle and a twist angle) and by the inclination of the colony boundary to the vertical plane. The results of this investigation will be presented and experimental and analytical difficulties encountered will be highlighted.

**10:10 AM**
**Micromechanical Modeling of Damage and Fracture in Lamellar Gamma-TiAl Alloys**: *Alfred Cornec*[1]; Malte Werwer[1]; [1]GKSS Research Center, Inst. for Matls. Rsrch., Max-Planck-Str. 1, Geesthacht 21502 Germany

A micromechanical multiscale finite element model is proposed for the simulation of the quasistatic damage and fracture behavior of lamellar gamma-TiAl alloys at room temperature. The model is based on a periodic unit cell for the lamellar substructure (PST-structure) of the colonies. The deformation behavior of the two phases alpha-2 and gamma is described by continuum crystal plasticity, and the clevage fracture behavior by a cohesive model. The PST-unit cell is validated by comparison with experimental data from compression and fracture tests of PST-specimens. The deformation and fracture behavior of the polycrystalline compound is simulated by multiscale finite element simulations which make use of the PST unit cells as material submodels. The results from the numerical simulations are compared with experimental data.

**10:30 AM**
**Studies of Dislocation and Twin Activities at Crack Tips in Near-Gamma Tial Using Electron Channeling Contrast Imaging**: *Boon-Chai Ng*[1]; Tom R. Bieler[1]; Martin A. Crimp[1]; [1]Michigan State University, Cheml. Eng. & Matls. Sci., 2527 Engineering, E. Lansing, MI 48824-1226 USA

Low toughness of titanium aluminides at ambient temperatures has prevented designers from using TiAl based alloys extensively in aerospace and automotive industries. Material toughness is typically associated with the ability to arrest cracks. Understanding how and why cracks propagate and arrest in these alloys will provide meaningful information for the improvement of toughness in these alloys. In this study, notched 4-point bend specimens of a near-gamma TiAl alloy were loaded in-situ in the SEM until a crack propagated from the notch root. Electron channeling contrast imaging (ECCI) was used to examine dislocation and twin activities in regions where the crack arrested or where microcracks nucleated. Observations indicate that nucleation of microcracks occurred ahead of the primary crack as a result of deformation twins impinging on grain boundaries with little or no strain transfer to the adjacent grain. Measurement of twin width and local strain generated by these twins indicates that microcracks tend t o form in conjunction with thicker twins that impose higher local strains at the boundary when there is poor compatibility of twins with deformation systems in adjacent grains. This work was supported by the Air Force Office of Scientific Research under # AFRL no. F49620-01-1-0116, monitored by Dr. Craig Hartley, and by the Michigan State University Composite Materials Structures Center.

**10:50 AM Invited**

**The Influence of Microstructure and Surface Residual Stresses on Pre-Yield Cracking in TiAl Alloys**: *Xinhua Wu*[1]; Dawei Hu[1]; Mike H. Loretto[1]; [1]University of Birmingham, IRC in Matls., Edgbaston, Birmingham B15 2TT UK

The tendency for fully lamellar samples of TiAl alloys to crack at stresses well below their macroscopic yield stress has been demonstrated in recent work and because this pre-yield cracking has been found to act as failure initiation sites during subsequent fatigue testing a major programme is underway to increase our understanding of this phenomenon. A number of TiAl-based alloys are being assessed to determine the influence of microstructure, of surface finish and of the nature and level of residual surface stresses on the extent of pre-yield cracking during tensile testing. At this stage it has been shown that both the microstructure and surface finish are important and work is underway to relate these observations to the extent of residual stresses in machined, polished and in shot-peened samples in three TiAl alloys which have very different microstructures. This work will be reported.

**11:20 AM**

**Incorporating Damage Tolerance Considerations to Aid the Insertion of Gamma Titanium Aluminides in Fracture-Critical Applications**: *James M. Larsen*[1]; Andrew H. Rosenberger[1]; Kezhong Li[2]; Reji John[1]; William J. Porter[2]; [1]Air Force Research Laboratory, AFRL/MLLMN, 2230 Tenth St., Ste. 1, WPAFB, OH 45433-7817 USA; [2]University of Dayton Research Institute, 300 College Park, Dayton, OH 45469 USA

Effective and timely transition of gamma titanium aluminides into fracture-critical components in turbine engines will require the cooperation of numerous organizations in the industry and government. This presentation explores the role of damage tolerance considerations for key fatigue-limited engine components, and discusses opportunities and impediments for material insertion. Data from the gamma TiAl alloy K5 (Ti-46.5Al-3Nb-2Cr-0.2W) are used to illustrate the role of the materialís resistance to fatigue crack initiation, small-crack growth, and fracture, with emphasis on the importance of understanding statistical variability in material properties and the relationship of this variability to microstructure. In many instances, understanding these relationships appears to hold the key to widespread acceptance of limited-ductility materials for use in fracture-critical applications.

**11:40 AM**

**Impact Resistance of Various Cast Gamma Alloys**: *Bradley A. Lerch*[1]; Susan L. Draper[2]; J. Michael Pereira[3]; Wyman Zhuang[4]; [1]NASA-GRC, 21000 Brookpark Rd., MS 49-7, Cleveland, OH 44135 USA; [2]NASA-GRC, MS 49-1, Cleveland, OH 44135 USA; [3]NASA-GRC, MS 49-8, Cleveland, OH 44135 USA; [4]Aeronautical and Maritime Research Laboratory, Airframes & Engines Div., Melbourne, Victoria 3207 Australia

This paper will present a summary of a six-year study on the impact resistance of cast gamma TiAl. Several gamma alloys (48-2-2, 47-2-2, ABB-2, ABB-23 and NCG) were ballistically impacted and variables such as impact energy, projectile hardness and impact location were related to the resulting damage. The goal was to produce damage that was similar to the domestic object damage found in low pressure turbine blades in aircraft engines. Damaged samples were subsequently tested under high cycle fatigue loading using the step-test method. The fatigue strength of each alloy was characterized as a function of initial crack size and successfully modeled using a threshold-based fracture mechanics approach. Differences among the various alloys will be discussed, particularly with respect to their tensile properties, fatigue limits and fatigue crack thresholds, and their affect on the impact damage and damage tolerance of each alloy.

**12:00 PM**

**Fracture Processes and the R-Curves for Fatigue Crack Propagation in Gamma-TiAl**: *Reinhard Pippan*[1]; Andreas Tesch[1]; Matthias Hˆck[2]; Manuel Beschliesser[3]; Heinrich Kestler[4]; [1]Austrian Academy of Sciences, Erich Schmid Inst. of Matls. Sci., Jahnstrasse 12, Leoben, Styria A-8700 Austria; [2]University of Leoben, Inst. of Metal Physics 8700 Austria; [3]University of Leoben, Inst. of Physl. Metall. & Matls. Testing 8700 Austria; [4]Plansee AG, Reutte A-6600 Austria

The fracture toughness as well as the fatigue crack propagation resistance exhibits strong R-curve behavior. The effect of microstructure was investigated in this study. The fracture toughness, the fatigue crack propagation behavior as well as the crack length dependence of these properties were studied in a coarse-grained designed fully lamellar, a fine-grained near Gamma and the corresponding aged microstructures (10.000 hours at 700∞C). In order to analyse the fracture process and to visualize the crack tip shielding mechanisms in situ fracture toughness tests in the scanning electron microscope were performed. The effect of microstructure and aging will be discussed.

**12:20 PM**

**High Temperature Assessment and Fracture of Gamma TiAl Intermetallics**: *Bilal Dogan*[1]; [1]GKSS Research Centre, Max-Planck-Str. 1, Geesthacht 21502 Germany

Development of unified lifing methodology for fracture critical components will provide assurance for new innovative constructions of gas turbines in choice of materials and/or fabrication methods and assurance in operation. Safe engine operation with extended component life and enhanced decision making processes is facilitated by validated defect assessment procedures. Guidelines and methodologies for high temperature defect assessment of conventional materials and in-house expertise exist in Europe and worldwide. Introduction of new materials, such as gamma based TiAl intermetallics, offer many potential benefits to gas turbine industry, though with lower ductility and fracture toughness than those of nickel based alloys. Hence, designers and manufacturers are challenged for their use in aero-engines, and by the operators in assessment of service performance and safe operation of TiAl components. Present paper reviews the defect assessment and lifing methodologies for high temperature fracture critical components. Fracture toughness and crack growth of gamma based TiAl intermetallics, Ti48Al2Cr and Ti47Al4.3(Cr,Mn,Nb,Si,B) alloys at 700∞C are reported. Creep deformation and crack growth behaviours are studied in an attempt to pave the way for developing a life assessment methodology for components made of advanced TiAl base intermetallic alloys.

## International Symposium on Intermetallic and Advanced Metallic Materials - A Symposium Dedicated to Dr. C. T. Liu: Intermetallics III–Multi-Phase Intermetallics

*Sponsored by:* ASM International: Materials Science Critical Technology Sector, Structural Materials Division, SMD-Mechanical Behavior of Materials-(Jt. ASM-MSCTS)

*Program Organizers:* Seetharama C. Deevi, Philip Morris USA, Research Center, Richmond, VA 23234 USA; Fritz Appel, GKSS Research Centre, Geesthacht D-21502 Germany; Robert W. Cahn, University of Cambridge, Materials Science and Metallurgy, Cambridge CB2 3QZ UK; Y. Austin Chang, University of Wisconsin-Madison, Department of Materials Science & Engineering, Madison, WI 53706-1595 USA; Guo Liang Chen, University of Science and Technology-Beijing, State Key Laboratory for Advanced Metals and Materials, Beijing 100083 China; Yip-Wah Chung, Northwestern University, Department of Materials Science & Engineering, Evanston, IL 60208-3108 USA; Shuji Hanada, Tohoku University, Sendai 980-8577 Japan; Linda Horton, Oak Ridge National Laboratory, Metals and Ceramics Division, Oak Ridge, TN 37831-6132 USA; Peter K. Liaw, University of Tennessee, Department of Materials Science and Engineering, Knoxville, TN 37996-2200 USA; Dong-Liang Lin, Shangai Jiao-Tong University, Shangai 200030 China; T. G. Nieh, Lawrence Livermore National Laboratory, Livermore, CA 94551 USA; Masaharu Yamaguchi, Kyoto University, Department of Materials Science & Engineering, Kyoto 606-8501 Japan

Tuesday AM — Room: 8
March 4, 2003 — Location: San Diego Convention Center

*Session Chairs:* Robert W. Cahn, University of Cambridge, Dept. of Matls. Sci. & Metall., Cambridge CB2 3QZ UK; Yip-Wah Chung, Northwestern University, Dept. of Matls. Sci. & Eng., Evanston, IL 60208-3108 USA

**8:30 AM Invited**

**Microstructure and Properties of Some High-Performance Thermo-Electric Compounds**: Lanting Zhang[1]; Kazuhiro Ito[1]; Haruyuki Inui[1]; *Masaharu Yamaguchi*[1]; [1]Kyoto University, Dept. of Matls. Sci. & Eng., Sakyo-ku, Kyoto 606-8501 Japan

The Seebeck effect was already used to generate electric energy in 19th century. However, widespread use of thermoelectric generators still requires rather drastic improvements over the properties of thermoelectric materials. In particular, a relatively low thermoelectric conversion efficiency should be improved. Recently, some intermetallic compounds with high ZT values have been found and their properties have been investigated. We prepared thin film and bulk specimens of ReSi2, Zn4Sb3 and some related materials, and measured their Seebeck coefficient, electrical resistivity and thermal conductivity in a wide temperature range. These properties vary with chemical composition, microstructure and whether specimens are in the film form or in the bulk form. The results of these investigations will be presented.

**8:50 AM Invited**

**Lattice Parameter Dependence on Long Range Ordered Degree in the Order-Disorder Transformation**: Xiaodong Ni[1]; *Guoliang Chen*[1]; Timothee Nsongo[2]; Nanxian Chen[2]; [1]University of Science & Technology-Beijing, State Key Lab. for Adv. Metals & Matls., Beijing 100083 China; [2]Tsinghua University, Dept. of Physics, Beijing 100084 China

The order-disorder transformations (ODT) of stoichimetrical Ni3Al, NiAl, and TiAl are studied by using Blagg-Williams (BW) model based on embedded atom method (EAM) atomic potential. It is a first order O-D transformation for Ni3Al while its second order O-D transformation for NiAl and TiAl alloys. The relation between the lattice parameter and the long-range order (LRO) parameter is proved to be linear for the first order transition such as Ni3Al and non-linear for the second order transition such as NiAl. The calculated linear lattice parameter dependence on LRO for Ni3Al is consistent with Cahnís experimental results. The calculated lattice parameter change proportionally corresponds to the change of the free energy of the ordered phase in the region of LRO from 0 to 1 for all alloys studied. The alternative distribution of pure Ti plane and pure Al plane in TiAl structure leads the strong directional d-bonding between nearest Ti atoms in pure Ti plane and the polarization of p-electrons at Al sites pointi ng directly along the [001] direction, resulting in an enhancement of the Ti-Al bonding. When LRO=0 the structure becomes fcc and the direction bonding is eliminated. As LRO increases, the lattice parameter a value and the volume of unit cell are reduced while the lattice parameter c value is increased.

**9:10 AM Invited**

**Atomic Processes and Phase Transitions in Complex Intermetallics: Quasicrystals**: *H.-E. Schaefer*[1]; F. Baier[1]; K. Sato[1]; W. Sprengel[1]; [1]Stuttgart University, Inst. of Theoretl. & Appl. Physics, Pfaffenwaldring 57, Stuttgart 70569 Germany

Quasicrystals are intermetallics with aperiodic structures and novel physical features. Their high temperature properties as atomic diffusion, plastic deformation etc. are controlled by atomic processes as vacancy formation and migration. As identified by specific techniques various types of vacancies (vacant atomic sites) were identified in quasicrystals: (i) Structural vacancies are available in quasicrystals and approximants; (ii) Thermal vacancies were studied at high temperatures; (iii) Vacancies can be induced by electron irradiation; where the nearest neighbour atoms can be characterized chemically. Structural phase transitions in quasicrystals could be detected for the first time on an atomic scale by positron annihilation techniques in the case of decagonal Al-Ni-Co at 1140 K. These data can be quantitatively correlated to order-disorder phenomena observed by neutron scattering.

**9:30 AM**

**Phase Equilibria in T-Al-C and T-Al-B Systems (T: Co, Rh and Ir) and Design of $E2_1$-$Co_3AlC$ Based Heat Resistant Alloys**: *Yoshisato Kimura*[1]; Kaoru Iida[1]; Fu-Gao Wei[1]; Yoshinao Mishima[1]; [1]Tokyo Institute of Technology, Matls. Sci. & Eng., Bldg. #G3-513, 4259 Nagatsuta, Midori-ku, Yokohama, Kanagawa 226-8502 Japan

We are interested in $E2_1$-$Co_3AlC$ as a high potential strengthener of Co-base heat resistant alloys since the $E2_1$ type ordered crystal structure is almost the same as that of the $L1_2$ type excluding that a carbon atom occupies the octahedral interstice at the body-center. To enhance the mechanical properties of the $E2_1$-$Co_3AlC$ based alloys, we have proposed the fourth element addition; rhodium and iridium substituting for the same 9 group element cobalt, and boron for carbon. It is also expected that microstructures would be thermally stabilized through modifying the lattice mismatch between (Co) and $E2_1$ phases. Objective of the present work is to investigate the phase equilibria in the transition metal corner of T-Al-C and T-Al-B systems (T: Rh and Ir), as to establish the basis of design on Co-base heat resistant alloys strengthened by $E2_1$-$Co_3AlC$. Phase diagrams have been experimentally determined for related alloy systems.

**9:45 AM**

**Phase Equilibria and Microstructures in the Fe-Si-Cr-Ti System**: *Hiroshi Usuba*[1]; Keisuke Yamamoto[1]; Yoshisato Kimura[1]; Yoshinao Mishima[1]; [1]Tokyo Institute of Technology, Dept. of Matls. Sci. & Eng., 4259 Nagatsuta, Midori-ku, Yokohama, Kanagawa-ken 226-8502 Japan

Iron-base alloys with the two-phase (disordered A2 + ordered $D0_3$) microstructure have received considerable attention as candidates for high temperature structural materials. The volume fraction, size and morphology of $D0_3$ phase can be controlled by heat treatments in Fe-Si-Cr system. Furthermore, by the Ti addition, it becomes possible to raise the order-disorder temperature and to expand the two-phase region. Effects of Si and Ti contents on microstructures and phase equilibria have been systematically investigated by transmission electron microscopy (TEM) for the alloys with constant Cr content fixed at 10at%. The Fe-Si-Cr alloys containing 12-15at% Si have the A2+$D0_3$ two-phase microstructure below about 873K. On the other hand, the Ti addition expands this two-phase region toward lower Si content at around 5at% and there exist (A2+$D0_3$+$L2_1$) three-phase region at around relatively higher Ti content. The morphology of $D0_3$ precipitates changes from plates to cuboids accompanying the precipitation of $L2_1$.

**10:00 AM**

**Design Strategies for Oxidation-Resistant Intermetallic and Advanced Metallic Alloys**: Michael P. Brady[1]; *Peter F. Tortorelli*[1]; Ian G. Wright[1]; Bruce A. Pint[1]; [1]Oak Ridge National Laboratory, MS 6115, Oak Ridge, TN 37831-6115 USA

This paper will discuss strategies for designing intermetallic and advanced-metallic alloys to form protective oxide scales. Emphasis will be placed on novel approaches based on manipulation of oxidation phenomena unique to multi-phase structures, either designed into the initial alloy microstructure or engineered to occur in-situ during subscale alloy depletion/enrichment processes. Factors which effect the maintenance of protective oxide scale formation will also be discussed. Examples will be drawn from studies of the oxidation behavior of Ti-, Fe-, and Ni- aluminides, Mo-based silicides, and Cr-based Laves phases conducted at Oak Ridge National Laboratory over the past decade.

**10:15 AM Break**

**10:35 AM**

**Nanointerfaces in High Performance Materials**: *R. V. Ramanujan*[1]; [1]Nanyang Technological University, Sch. of Matls. Eng., Nanyang Ave. 639798 Singapore

Interphase interfaces play a vital role in improving the structural and functional properties of a wide class of materials. Structural properties of advanced metallic systems have been vastly improved by nanoscale engineering of the properties of such interfaces. Functional properties, such as soft magnetic properties of nanomaterials, show that the interface between the nanoprecipitate and the matrix plays a crucial role in the crystallization behavior as well as in the optimization of the magnetic properties. The author has extended to a range of alloy systems the collaborative work on nanointerfaces performed by him with Dr. C.T. Liu. Two examples of the effect of interfaces on properties will be presented. First, experimental work using TEM, EDX, STEM and SEM on the stability of nanoscale interfaces in lamellar structures in the TiAl-X system will be reported, the modeling work examining the effect of the interfacial structure and composition on the stability of such interfaces will be discussed. The seco nd example will be the development of nanoscale soft magnetic precipitates using the Herzer diagram; this requires nanosized precipitates separated by nanoscale distances. Modeling work to determine the interfacial structure, composition and energy that will produce such materials will be presented. Corresponding experimental work, using TEM, EDX, DSC and resistivity, on heat treated iron and cobalt based alloys will also be presented. These examples will demonstrate the engineering importance of nanoscale interfaces.

**10:50 AM**

**Processing of Intermetallics for Improved Ductility, Toughness, and Superplasticity**: *Shankar M.L. Sastry*[1]; [1]Washington University, Mechl. Eng., CB 1185, One Brookings Dr., St. Louis, MO 63130 USA

Intermetallics literature indicates a definite trend of the beneficial effect of grain refinement on the low temperature ductility, fracture toughness, and yield strength, particularly when the grain size is reduced to less than 1μm. However, conventional thermo-mechanical processing of bulk intermetallics has not resulted in sub-micrometer sized grains. Nanograined intermetallics produced by powder processing routes, such as mechanical alloying and vapor phase synthesis, invariably have excessive contamination and incomplete densification. Thus, improvements both in ductility and toughness have not been realized using this type of nanoparticle powder processing approaches. Recent studies of the severe plastic deformation (SPD) processing by Equal Channel Angular Extrusion (ECAE) of titanium-, nickel, and iron aluminides indicate that the SPD processing is a viable method for producing ultra fine grain structures in bulk intermetallics and holds promise for improving the room temperature ductility and toughness and high temperature superplasticity of intermetallics.

**11:05 AM Invited**
**Formation of Point Defects in TiAl and NiAl**: Yulin Hao[1]; *Rui Yang*[1]; Yan Song[2]; Yuyou Cui[1]; Dong Li[1]; Mitsuo Niinomi[3]; [1]Chinese Academy of Sciences, Inst. of Metal Rsrch., Titanium Alloy Lab., 72 Wenhua Rd., Shenyang 110016 China; [2]Queen Mary, University of London, Dept. of Matls., Mile End Rd., London E1 4NS UK; [3]Toyohashi University of Technology, Dept. of Production Sys. Eng., 1-1, Hibarigaoka, Tempaku-cho, Toyohashi 441-8580 Japan

A mean-field model is proposed to estimate the atom-atom and atom-vacancy bond energies of intermetallic compounds, with the results of first principles calculations as input. The distribution and variation of point defects with temperature and chemical composition estimated with the model agreed with experimental measurements for TiAl and NiAl alloys. In particular, off-stoichiometric effects on the concentration of point defects are considered in this treatment. Compared to previous models that neglect the off-stoichiometric effects, our theoretical study suggests lower vacancy concentrations in Al-rich alloys but higher vacancy concentrations on the Ti-rich side. As a result, the differences in vacancy concentration between Al-rich and Al-lean TiAl alloys are less than those reported in previous studies. Constitutional vacancies are present but anti-site defects are forbidden in Al-rich NiAl at 0 K. For concentrated Al-rich NiAl, the vacancy concentration has its maximum at 0 K, and gradually decreases with rising temperature until diffusion is activated.

**11:25 AM**
**A New Ru-Rich Heusler Phase**: *Q. Feng*[1]; T. K. Nandy[1]; B. Tryon[1]; T. M. Pollock[1]; [1]University of Michigan, Dept. of Matls. Sci. & Eng., 2300 Hayward St., Ann Arbor, MI 48109 USA

An ordered $L2_1$ Heusler phase based on the $Ru_2AlTa$ composition has been identified by X-ray diffraction and electron diffraction analysis in a high Ru-containing multicomponent superalloy. Such a phase has not been previously observed in Ni-base superalloys or as a bulk intermetallic. In order to study the effect of this phase on mechanical properties of multiphase superalloys, two compositions based on this Heusler phase have been melted for the evaluation of flow behavior in compression as a function of temperature. The mechanical behavior of these $Ru_2AlTa$ intermetallic alloys will be discussed in comparison to other Ru-containing intermetallics.

**11:40 AM**
**Microstructural Design of a Wrought Ni-Base Superalloy for Improved Resistance Against Environmental Embrittlement**: *Joachim Roesler*[1]; Dominique Del Genovese[1]; Martin Goetting[1]; Debashis Mukherji[1]; Pavel Strunz[2]; Ralf Gilles[3]; [1]Technical University Braunschweig, Inst. f¸r Werkstoffe, Langer Kamp 8, Braunschweig 38106 Germany; [2]Nuclear Physics Institute, Rez 25068 Czech Republic; [3]Technische Universit‰t Darmstadt, Petersenstrasse 23, Darmstadt 64287 Germany

The wrought Ni-Fe base superalloy Inconel 706 is of particular interest as disc material for land based gas turbines because of its balanced manufacturability and elevated temperature strength. It is also under consideration for ultra high temperature steam turbine applications with prospective steam inlet temperatures of about 700∞C. Due to the operation conditions of these advanced machines and the damage tolerant design philosophy, satisfactory creep crack growth resistance at temperatures beyond 600∞C is of paramount importance. However, Inconel 706 suffers from environmental embrittlement of the grain boundaries as other comparable alloys do, leading to fast creep crack growth and brittle intergranular fracture at the above mentioned temperature range. It will be demonstrated here that careful design of the microstructure by slight adjustment of the heat treatment cycle used today is capable of reducing the creep crack growth rate by several orders of magnitude. The reasons for this drastic effect are el ucidated by detailed microstructural analysis. ìLockingî of the grain boundaries by discontinuous precipitation of the ?-phase turns out to be the most relevant aspect. As this precipitation process happens in competition to other precipitation reactions in the grain interior (in particular: ?¥/? ¥¥-formation), it sensitively depends on the thermal history. Interrupted heating experiments and in-situ neutron scattering are used to explain these interdependencies. Based on these findings, a modified heat treatment cycle for improved resistance of Inconel 706 against environmental embrittlement is suggested. It is particularly well suited for large forgings as it employs slow cooling from the solutioning temperature.

**11:55 AM**
**Oxidation Behavior of Aluminide Alloys in the Operating Temperatures of Solid Oxide Fuel Cells**: *Weizhong Zhu*[1]; Seetharama C. Deevi[1]; [1]Philip Morris USA, R&D Ctr., 4201 Commerce Rd., Richmond, VA 23234 USA

Several different iron aluminde alloys have been investigated as potential interconnects for intermediate temperature solid oxide fuel cell (SOFC) stack, i.e., operating below 800°C. Properties of paramount importance such as oxidation resistance, contact resistance of the scale, and thermal expansion were examined. Emphasis is put on a comparative study of the oxidation behavior of aluminide alloys and stainless steels. Oxide scales of the alloys exposed to air in the temperature range of 600-800°C for up to 1000hr were identified by X-ray diffraction. The predominant scale of alloys oxidized at 800°C for 1000hr is either iron nitride or aluminum nitride with a minor amount of alumina. Oxidation behavior was investigated in an attempt to predict the long-term response of the alloys in real SOFC atmospheres. Contact resistances of iron aluminides and stainless steels were compared after extended periods of oxidation. We discuss our comparisons and discuss the potential of iron aluminides for interconnect applications.

**12:10 PM Invited**
**Laves PhasesñStructure and Stability**: *Frank Stein*[1]; Martin Palm[1]; Gerhard Sauthoff[1]; [1]Max-Planck-Institut fuer Eisenforschung, Physl. Metall., Max-Planck-Str. 1, Duesseldorf 40237 Germany

Laves phases form the largest group of intermetallic phases. Although they are well known since long, there are still unsolved problems concerning the stability of the respective crystal structures. The Laves phases crystallize with a cubic $MgCu_2$-type structure or a hexagonal $MgZn_2$-type or $MgNi_2$-type structure which differ only by the particular stacking of the same four-layered structural units. It is still not possible to predict which of the possible structure types is the stable one for a Laves phase compound $AB_2$. Phase transformations from a cubic low-temperature structure to a hexagonal high-temperature structure were observed as well as stress-induced transformations from the hexagonal structure to the cubic one. In addition, deviations from the stoichiometric composition were reported to result in a change of the stable structure for various systems. Existing models using geometrical and electronic factors for predicting the occurrence and the structure type of a Laves phase are reviewed. On the basis of extensive experimental results obtained for various binary and ternary alloy systems the applicability of the different models to real systems is checked and existing problems are demonstrated.

## International Symposium on Structures and Properties of Nanocrystalline Materials: Mechanical Properties II

*Sponsored by:* Structural Materials Division, Electronic, Magnetic & Photonic Materials Division, SMD-Mechanical Behavior of Materials-(Jt. ASM-MSCTS), Jt. EMPMD/SMD-Chemistry & Physics of Materials Committee
*Program Organizers:* Sung H. Whang, Polytechnic University, Department of Mechanical Engineering, Brooklyn, NY 11201 USA; Robert D. Shull, NIST, Magnetic Materials, Gaithersburg, MD 20899-8552 USA

Tuesday AM — Room: 14B
March 4, 2003 — Location: San Diego Convention Center

*Session Chairs:* Harriet Kung, US Department of Energy, Office of Basic Energy Scis., Germantown, MD 20874 USA; Ennio Bonetti, University of Bologna, Dept. of Physics & INFM, Bologna 40127 Italy

**8:30 AM**
**Theoretical and Experimental Investigation of the Indentation Size Effect with Spherical and Pyramidal Indenters**: J. G. Swadener[1]; *E. P. George*[2]; G. M. Pharr[3]; [1]Los Alamos National Laboratory, Matls. Sci. & Tech. Div., PO Box 1663, Los Alamos, NM 87545

USA; [2]Oak Ridge National Laboratory, Metals & Ceram. Div., 1 Bethel Valley Rd., Oak Ridge, TN 37831-6093 USA; [3]University of Tennessee, Dept. of Matls. Sci. & Eng., Knoxville, TN 37996 USA

When tested in small volumes, metals and polymers often show dramatic increases in strength compared to their macroscopic strength. Thus, for example, when hardness is measured with pyramidal indenters, an increase in hardness is observed with decreasing depth of penetration, with the effect becoming apparent at depths less than a few microns. Recently we have shown that a similar size effect exists also in spherical indentation. However, it is manifested not through the depth of indentation but rather through the radius of the indenter; significant increases in hardness are observed as the radius of the indenter is reduced. A model based on geometrically necessary dislocations was developed for spherical indentation which agrees with the experimental results for all but the smallest indent used in our study. The primary advantage of spherical indentation is that size effects and work hardening effects can be de-coupled and determined separately unlike in the case of sharp indenters. Research at the Oak Ridge National Laboratory SHaRE Collaborative Research Center was sponsored by the Division of Materials Sciences and Engineering, US Department of Energy, under contract DE-AC05-00OR22725 with UT-Battelle, LLC. Additional funding was supplied by the US Department of Energy Office of Basic Energy Science under contract W-7405-Eng-36.

**9:00 AM**

**Characterization and Mechanical Properties of Sputter-Deposited $Ni_3Al$ Thin Films**: *Evan Andrew Sperling*[1]; Arda Genc[1]; Rajarshi Banerjee[1]; Peter M. Anderson[1]; Hamish L. Fraser[1]; [1]The Ohio State University, Matls. Sci. & Eng., 2041 College Rd., Columbus, OH 43210 USA

Monolithic thin films of stoichiometric $Ni_3Al$ were prepared by UHV magnetron sputtering from an alloy target. Deposition at room temperature on oxidized Si wafers produced nanocrystalline $Ni_3Al$ oriented in the (111) direction. The size of the nanocrystalline grains was studied as a function of deposition parameters by means of X-Ray diffraction and TEM. As the Ar sputtering pressure was increased from 5 mTorr to 100 mTorr, the deposition rate and grain size decreased. Elevated temperature deposition with the substrate pre-baked and held at 400∞C produced larger grains and a chemically ordered $Ni_3Al$ phase. The hardness and modulus of the nanocrystalline films are being measured using nanoindentation and the relationship between structure and properties will be discussed in this paper. Furthermore, the mechanical properties of the nanocrystalline films will be compared to the properties of bulk $Ni_3Al$ alloys.

**9:20 AM**

**Effects of Decreasing Layer Thickness on the High Temperature Mechanical Properties of Copper Based Nanoscale Multilayers**: *Nathan Allan Mara*[1]; Daniel Coyle[1]; Alla Sergueeva[1]; Amit Misra[2]; Amiya Mukherjee[1]; [1]University of California-Davis, Cheml. Eng. & Matls. Sci., One Shields Ave., Davis, CA 95616 USA; [2]Los Alamos National Laboratory, Matls. Sci. & Tech. Div., MS G755, Los Alamos, NM 87545 USA

Nanometer-scale polycrystalline multilayered films (with layer thickness less than 100 nm) typically exhibit high yield strength, often approaching the theoretical strength at room temperature. However, 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-based multilayers (Cu/Ni and Cu/Nb) at diminishing length scales were investigated. Free-standing samples were tested in uniaxial tension at temperatures ranging from 25 to 700°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 mechanisms. This investigation is supported by NSF, Division of Materials Research, grant NSF-DMR-9903321.

**9:40 AM**

**Plastic Behavior of Nanocrystalline Fe Powder Formed by Mechanical MillingñA Nanoindentation Study**: *Dongchan Jang*[1]; Michael Atzmon[2]; [1]University of Michigan, MSE, 3062 H. H. Dow Bldg., Ann Arbor, MI 48109-2136 USA; [2]University of Michigan, NERS & MSE, Cooley Bldg./N. Campus, Ann Arbor, MI 48109-2104 USA

Numerous authors have reported on the so-called ìinverse Hall-Petchî effect, namely the decrease of hardness with decreasing grain sizes when the latter are of the order of a few nanometers. This effect has been controversial because many synthesis methods result in porous samples, thus introducing artifacts into hardness measurements. In the present study, we report on nanoindentation hardness measurements, conducted on a scale smaller than the particle size. The grain sizes of our samples have been well characterized by the Warren-Averbach analysis. We observe a hardness increase with decreasing grain size to dimensions below those previously reported, suggesting potential artifacts in past studies. Below 18 nm, a slight hardness decrease is observed. We have also measured the strain-rate sensitivity, and found it to increase with decreasing grain size, suggesting the possibility of grain-boundary sliding at room temperature.

**10:00 AM Break**

**10:20 AM**

**Superplastic Behavior of As-Equal Channel Angular Pressed 5083 Al Alloys**: *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. & Matl. Sci., 1271, Sa 1-Dong, Ansan, Kyunggi-Do 425-791 S. Korea

A submicrometer grained structure was introduced into the two grades of the 5083 Al alloys, one containing 0.2 wt.% of Sc and the other without Sc, and their superplastic behavior was investigated. For the alloy without Sc, low temperature superplasticity was obtained while high strain rate superplasticity was possible in the alloy containing Sc. The characteristics of low temperature and/or high strain rate superplasticity of the alloys were discussed in view of microstructural evolution during equal channel angular pressing and subsequent deformation.

**10:40 AM**

**Variation of Mechanical Properties and Texture Development in Copper and Aluminium Under ECAP**: *Ralph J˚rg Hellmig*[1]; Yuri Estrin[1]; Seung Chul Baik[2]; Min Hong Seo[3]; Hyoung Seop Kim[3]; [1]Technische Universit‰t Clausthal, Inst. f¸r Werkstoffkunde und Werkstofftechnik, Agricolastr. 6, Clausthal-Zellerfeld 38678 Germany; [2]Pohang Iron & Steel Company, Ltd., Techl. Rsrch. Labs., Pohang 790-785 Korea; [3]Chungnam National University, Dept. of Metallurgl. Eng., Daejeon 305-764 Korea

In this talk we compare the mechanical, microstructural and textural variations during the four well known routes (A, BA, BC and C) of equal channel angular pressing (ECAP) of 99.9% purity copper and technical purity aluminium. Strength and tensile ductility of the ECAP processed materials were determined as a function of the number of pressings. In addition, TEM investigations were carried out to resolve the cell structure formed as a result of ECAP. The texture evolution for all processing routes was determined by X-ray diffraction. The results obtained were used to verify a dislocation based constitutive model that combines a two-internal variable approach with crystal plasticity. The model was shown to give a very good prediction of microstructural evolution, texture development and variation of thetensile strength of the materials studied.

**11:00 AM**

**Deformation Twins in Titanium Processed by Equal Channel Angular Pressing**: *Jongryoul Kim*[1]; Inyoung Kim[1]; SooHyun Han[1]; *Yong-Seog Kim*[2]; *Dong Hyuk Shin*[1]; [1]Hanyang University, Metall. & Matls. Sci., Ansan, Kyungggi-do 425-791 Korea; [2]Hong Ik University, Matls. Sci. & Eng., Seoul 121-791 Korea

After the first pass of ECAP at 623 K, the microstructure of pure titanium was composed of {10 1} deformation twin bands, rather than dislocation slip bands. This result raises an interesting question on characteristics of the twins developed during ECAP. Maximum shear strain that can be accommodated by deformation twin in most of HCP metals is in a range from 0.13 to 0.22. This strain is much smaller than the strain imposed by ECAP, ~1.83. This indicates that the twinning modes developed in pure Ti by the ECAP might be significantly different from the conventional twinning modes. In this respect, HREM analysis was conducted to investigate the atomic structure of {10 1} twin. The analysis revealed that various twinning modes such as the b1, b2 and b3 mode occurred in the sample. These modes can accommodate much lager deformation in comparison with the conventional b4 mode.

## Lead-Free Solders and Processing Issues Relevant to Microelectronics Packaging: Fundamentals, Phases, Wetting and Solidification

*Sponsored by:* Electronic, Magnetic & Photonic Materials Division, EMPMD-Electronic Packaging and Interconnection Materials Committee
*Program Organizers:* J. P. Lucas, Michigan State University, Chemical Engineering and Materials Science, East Lansing, MI 48824 USA; Srini Chada, Motorola, Department APTC, Plantation, FL 33322 USA; Sung K. Kang, IBM, T. J. Watson Research Center, Yorktown Heights, NY 10598 USA; C. Robert Kao, National Central University, Department of Chemical and Materials Engineering, Chungli City 32054 Taiwan; Kwang-Lung Lin, National Cheng Kung University, Department of Materials Science and Engineering, Tainan 70101 Taiwan; Jud Ready, MicroCoating Technologies, Atlanta, GA 30341 USA; Jin Yu, KAIST, Center for Electronic Packaging Materials 305-701 Korea

Tuesday AM — Room: 15B
March 4, 2003 — Location: San Diego Convention Center

*Session Chairs:* James P. Lucas, Michigan State University, Cheml. Eng. & Matls. Sci., E. Lansing, MI 48824 USA; Srinivas Chada, Motorola, Dept. APTC, Plantation, FL 33322 USA

**8:30 AM Invited**
**Ag3Sn Plate Formation in the Solidification of Near Ternary Eutectic Sn-Ag-Cu Alloys**: *Sung K. Kang*[1]; Won K. Choi[1]; Da-Yuan Shih[1]; Donald W. Henderson[2]; Timothy Gosselin[2]; Amit Sarkhel[2]; Charles Goldsmith[3]; Karl J. Puttlitz[3]; [1]IBM, T. J. Watson Rsrch. Ctr., Yorktown Heights, NY 10598 USA; [2]IBM Corporation, 1701 North St., Endicott, NY 13760 USA; [3]IBM Corporation, Hopewell Junction, NY 12533 USA

Near ternary eutectic Sn-Ag-Cu alloys, such as Sn-3.8Ag-0.7Cu (wt.%), are leading candidate solders to replace the Sn-Pb eutectic solder in the transition to Pb-free soldering technology. This alloy system has three solid phases - b (Beta) Sn, Ag3Sn and Cu6Sn5. In the solidification of near eutectic Sn-Ag-Cu alloys, the equilibrium eutectic transformation is kinetically inhibited. While the Ag3Sn phase nucleates with minimal undercooling, the b-Sn phase requires a typical undercooling of 15 to 25∞C for nucleation. As a consequence of this disparity in the required undercooling for nucleation, large Ag3Sn, plate-like, structures can grow rapidly within the liquid phase, during cooling, before the final solidification of solder joints. At lower cooling rates, the large Ag3Sn plates can subtend the entire cross section of solder joints and can grossly influence the mechanical deformation behavior of such solder joints under thermomechanical fatigue conditions. It is demonstrated that the Ag3Sn plate formation can be suppressed kinetically by utilizing elevated cooling rates or suppressed thermodynamically by using reduced Ag compositions.

**8:55 AM**
**Solidification of Eutectic and Near-Eutectic Alloys in the Ag-Cu-Sn System**: Leonid Snugovsky[1]; *Doug D. Perovic*[1]; John Rutter[1]; [1]University of Toronto, Matls. Sci. & Eng., Wallberg Bldg., 184 College St., Toronto, Ontario M5S 3E4 Canada

The techniques of DSC, quenching of samples during freezing and slow unidirectional solidification were used to evaluate the ternary eutectic temperature, composition and freezing characteristics of the Ag-Cu-Sn system. The eutectic temperature was determined to be 217+/- 0.4°C at a composition of 3.5 wt% Ag, 0.9 wt% Cu , balance Sn. The ternary eutectic was found to be of the faceted (Ag3Sn) faceted (Cu6Sn5) nonfaceted (Sn) type. The Ag3Sn phase forms a broken lamellar microstructure while the Cu6Sn5 phase forms a fibrous microstructure: the fibers become hollow hexagonal prisms at very low growth rates. The volume fraction occupied by the two compound phases, taken together, was measured as 5.5+/-0.5 and calculated as 5.63 vol.%. The compound phases are very poor nucleation catalysts for Sn, an effect that can result in the formation of Sn dendrites even from a melt of eutectic composition. When fractured, both compound phases showed brittle behaviour.

**9:15 AM**
**In Situ Observation and Simulation of Solidification Process in Soldering SOP with Sn-Ag-Cu Lead-Free Alloy**: Motoharu Haga[1]; Keun-Soo Kim[1]; *Katsuaki Suganuma*[1]; [1]Osaka University, Inst. of Scientific & Industl. Rsrch., Mihogaoka 8-1, Ibaraki, Osaka 567-0047 Japan

In soldering, because cooling speed depends on a design of assemblies and material properties of components, especially lead frame alloys such as 42 alloy and Cu, the formation of defects on solidification will be strongly influenced by those factors. In the present study, solidification process of SOP joint (42 alloy and Cu lead frame) was analyzed by the in situ observation combined with solidification simulation. In situ and microstructural observations of the circuit boards with a SOP soldered with Sn-3wt%Ag-0.5wt%Cu were carried out. The $\beta$-Sn dendrite structure in the solder fillet of a SOP with 42 alloy lead frames is larger compared with that of a Cu lead frame one. This is attributed to the slower cooling speed of 42 alloy lead frame SOP than that of Cu lead frame one. The solidification for a SOP joint is not uniform and locally time dependent. The solder surface of slowly cooled region of the 42 alloy lead frame SOP exhibited solidification cracks and rough surface by coarsening the dendrite structure. According to the simulation of solidification process, the relationship between solidification process and formation characteristics of solidification defects for a SOP joint can be clarified. The experimental results explained well by the simulation of solidification process.

**9:35 AM**
**Effects of Impurities on Phase Equilibria and Reactivity of Near Eutectic Sn-Ag-Cu Solder**: *Jaeyong Park*[1]; Rajendra Kabade[1]; Choong-Un Kim[1]; Ted Carper[2]; Puligandla Viswam[3]; [1]The University of Texas at Arlington, Matls. Sci. & Eng., 500 W. 1st. St., Woolf Hall, Rm. 325, Arlington, TX 76019 USA; [2]Nokia Mobile Phones, Inc., Rsrch. & Tech. Access, 6000 Connection Dr., MS 2:3207, Irving, TX 75039 USA; [3]Nokia Mobile Phones, Inc., Rsrch. & Tech. Access, 6000 Connection Dr., MS 2-200, Irving, TX 75039 USA

Among various Pb-free solders, Sn-Ag-Cu (ACS) alloys with near eutectic composition are considered the most attractive replacement for Pb-Sn solders and are in fact used in a few selected cases. Owing to its practical importance, numerous studies have been conducted on ACS alloys in order to understand their properties as a solder, including microstructural characteristics, wettability to various UBM schemes, and mechanical reliabilities. In practical applications, however, a solder system is not free from contaminants because it is forced to be in contact with lead-frame or substrate. A small amount of contaminants introduced in the ACS system may induce a substantial change in the phase equilibria and various related properties, and, therefore its influence needs to be investigated. This study presents the influence of several elements introduced into near eutectic ACS system on its phase equilibria and reactivity with Cu substrate. The elements investigated include Au, Co, Fe, Ni, Pb and Pd.

**9:55 AM**
**Effect of Polyethylene Glycol Residues on the Reliability of Printed Wiring Boards**: Jason P. Pilon[2]; *Laura J. Turbini*[1]; [1]University of Toronto, Ctr. for Microelect. Assem. & Pkgg., 184 College St., Rm. 150B, Toronto, Ontario M5S 3E4 Canada; [2]University of Toronto, Dept. of Matls. Sci. & Eng., 184 College St., Rm. 140, Toronto, Ontario M5S 3E4 Canada

Polyethylene glycol (PEG) is a common constituent of water-soluble flux. Zado first investigated the effect of PEG on the surface insulation resistance (SIR) of comb patterns soldered with PEG-containing flux. After SIR testing he examined the boards using SEM and noted lead residues between anode and cathode. He ascribed the low SIR readings to interaction between PEG and the epoxy substrate. Later, Brous proved that PEG was present in the epoxy and developed a chemical extraction process using acetonitrile. Recently, Bent studied the effect of PEG containing fluxes on SIR using copper-metallized comb patterns. For the formulation containing PEG without activators, he observed a silvery residue between comb fingers. Although these residues were not dendritic in nature, it was shown by SEM/EDS to contain copper. This paper will characterize and identify the chemistry that leads to these residues.

**10:15 AM Break**

**10:25 AM Invited**
**Horizontal and Vertical Flow of Molten Pb-Free Solders Along V-Grooves on Si**: *King-Ning Tu*[1]; [1]University of California-Los Angeles, 405 Hilgard Ave., Los Angeles, CA 90095-1595 USA

V-grooves of 100 micron in width, along the [110] directions on (001) Si wafer surfaces, were etched by lithographic technique. They were coated with Cr/Cu thin films. When a bead of molten solder was dropped on a V-groove which was placed horizontally, the melt ran along the V-groove and obeyed the Washburn model with a parabolic rate of motion. The rate was measured with a CCD camera. When the V-groove was dipped vertically into a pot of molten solder, the solder climbed up the V-groove to a certain height due to the capillary effect. Combining these measurements and the measurement of wetting angles of a solder cap on a flat Cu/Cr/Si surface, we attempted to analyze the surface tension and viscosity of the molten Pb-free solder. A comparison of the wetting behaviors of Pb-free solders with eutectic SnPb solder has been made. The effect of interfacial intermetallic compound formation on the wetting behavior will be discussed.

**10:50 AM**
**Phase Equilibria of Au-In-Sb-Sn Lead-Free Solder Alloys**: Jin Zhanpeng[1]; K. Ishida[2]; Liu Huashan[1]; Wang Chong[1]; Wang RiChu[1]; *Liu Chunlei*[1]; [1]Central South University, Ctr. of Phase Diagram & Matls. Design, Sch. of Matls. & Eng., Changsha, Hunan 410083 China; [2]Tohoku University, Dept. of Matls. Sci., Grad. Sch. of Eng., Sendai 980-8579 Japan

Phase relations in the Au-In-Sb-Sn quaternary system, the most basic information necessary for the development of lead-free solder alloys, were studied using the CALPHAD (CALculation of PHAse Diagrams) technique. Gibbs energies describing the constituent phases were obtained by optimizing the obtained data on the experimental phase diagrams and thermodynamics properties. The thermodynamic database of this multi-component system provides various information on phase equilibria such as liquidus and solidus surface, isothermal and vertical sections, mole fractions of the phase constituents, etc., and thermodynamics properties such as heat of mixing, surface energy, etc., of related liquid alloys in this multi-component lead-free solder system. Typical examples for the phase diagrams and thermodynamics properties of Au-In-Sb-Sn quaternary system are calculated. Some experiments were also carried out to get some phase equilibria information of this quaternary system and verify the reasonableness of the thermodynamics database of this quaternary system and its constituent ternary and binary systems.

**11:10 AM**
**Chemical Reactions that Lead to Conductive Anodic Filament Formation**: Laura J. Turbini[1]; *Antonio Caputo*[1]; [1]University of Toronto, Ctr. for Microelect. Assem. & Pkgg., 184 College St., Rm. 150B, Toronto, ON M5S 3E4 Canada

Conductive Anodic Filament (CAF) is a failure mode in printed wiring boards (PWBs) which occurs under high humidity and high voltage gradient conditions. The filament, a copper salt, grows from anode to cathode along the epoxy-glass interface. In there recent work, Ready and associates have identified CAF to be an atacamite-like insoluble compound, $Cu_7Cl_4(OH)_{10}\sum H_2O$, with semiconductor-like properties. The natural occurring form of atacamite has been identified to be $Cu_2Cl(OH)_3$. Meeker and LuValle have proposed a general kinetic model to describe the chemical reactions, which lead to reliability failures in PWBs. Using this model, the various chemical processes that are involved in the formation of CAF in processed PWBs will be analyzed and defined, using various analytical techniques. This paper will define the chemical reactions that result in the formation of CAF.

**11:30 AM**
**An Investigation of Addition of Copper Nanopowders on Microstructure, Microhardness and Solderability of Sn-3.5%Ag Solder Wetting on Copper Substrate**: *D. C. Lin*[1]; T. M. Guo[1]; *G.-X. Wang*[1]; T. S. Srivatsan[1]; [1]The University of Akron, Dept. of Mechl. Eng., 302 E. Buchtel Mall, Akron, OH 44325-3903 USA

Eutectic Sn-3.5%Ag solder is a potentially attractive and economically viable alternative to replace lead-containing solders. In this research investigation, a series of experiments on solder/copper substrate couple were conducted with the objective of examining the influence of nano-sized copper powders on strength and performance of the eutectic Sn-3.5% Ag solders. Even addition of small percentages was found to improve strength. The strength increase is rationalized as being due to the presence and distribution of the intermetallic compound both within the solder matrix and at interfaces of the solder/copper substrate coupled with refining of the eutectic solder. Examination of the microstructure revealed that addition of copper powders refined the primary tin-rich phase in the solder matrix while concurrently refining the size of the intermetallic compound present at and along the solder substrate interface. Addition of nanopowders of copper has a positive effect on the solderability of composite solder when compared to the addition of micron sized copper powder. This presentation will highlight salient features pertaining to thermal characteristics during solidification, microstructure development, microhardness and the role of nanoparticle addition on tinósilver solder/copper substrate couple.

**11:50 AM**
**Novel Ultrasonic Soldering Method for Lead-Free Solders**: *Keitaro Kago*[1]; Kenji Ishida[2]; Toshihisa Horiuchi[2]; Kazumi Matsushige[2]; Shiomi Kikuchi[3]; Kenichiro Suetsugu[4]; Shunji Hibino[5]; Takashi Ikari[4]; [1]Kyoto University, Venture Business Lab., Yoshidahonmachi, Sakyo-ku, Kyoto 606-8501 Japan; [2]Kyoto University, Grad. Sch. of Eng., Yoshidahonmachi, Sakyo-ku, Kyoto 606-8501 Japan; [3]The University of Shiga Prefecture, Dept. of Matls. Sci., 2500 Hassaka-cho, Hikone, Shiga 522-8533 Japan; [4]Matsushita Electric Industrial Company, Ltd., Environml. Production Eng. Lab., 2-7 Matsuba-cho, Kadoma, Osaka 571-8502 Japan; [5]Matsushita FA Engineering Company, Ltd., 2-7 Matsuba-cho, Kadoma, Osaka 571-8502 Japan

The Sn-Bi solder has good prospects for the future as the low temperature type lead-free solder. But its wettability on the copper land is low and the bonding strength is weak. It is due to the segregation of Bi needle-like microcrystalline at the bonded interface. We found that the application of ultrasound improved the mechanical strength of Sn-Bi solder. It is because the ultrasound miniaturized the microcrystallines of Bi to form the interfacial layer. Moreover, we invented newly the ultrasonic soldering apparatus. By using it, we can apply the ultrasound to the printed wire board (PWB). The temperature of PWB increased above the melting point of Sn-58Bi solder and the solder paste melted only by ultrasound without other heating method. The wettability was improved. It may be because the ultrasound miniaturized the microcrystallines. The technique we invented will improve the usability and reliability of Sn-Bi solders.

**12:10 PM**
**Surface Tension and Density Measurements of Sn-Ag-Sb Liquid Alloys, Phase Diagram Calculations and Modeling**: *Z. Moser*[1]; W. Gasior[1]; Janusz Pstrus[1]; X. J. Liu[2]; I. Ohnuma[2]; K. Ishida[2]; [1]Polish Academy of Sciences, Inst. of Metall. & Matls. Sci., Reymonta St. 25, Krakow 30-059 Poland; [2]Tohoku University, Dept. of Matls. Sci., Grad. Sch. of Eng., Aoba-yama 02, Sendai 980-8579 Japan

The maximum bubble pressure method has been used to measure the surface tension of pure Sb, surface tension and density (dilatometric method) by adding to (3.8 at.% Ag-Sn) eutectic 0.03, 0.06 and 0.09 molar fractions of Sb at the temperature range 2770C to 9770C. The linear dependencies of densities and surface tensions on temperature were observed and they were described by straight-line equations. Moreover, a phase diagram calculations were performed and the resulting optimised thermodynamic parameters were used for modeling of the surface tension. In addition, a non-equilibrium solidification process using the Scheil model was simulated and compared with the equilibrium solidification behaviour in some Sn-Ag-Sb base alloys.

## Magnesium Technology 2003: Magnesium Casting and Solidification and Simulations

*Sponsored by:* Light Metals Division, Materials Processing and Manufacturing Division, LMD-Magnesium Committee, International Magnesium Association, MPMD-Solidification Committee
*Program Organizers:* Howard I. Kaplan, US Magnesium LLC, Salt Lake City, UT 84116 USA; Menachem Bamberger, Technion, Israel Institute of Technology, Haifa 32000 Israel; John L. Mihelich, Metal Experts International, Winston, GA 30187 USA

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|---|---|
| Tuesday AM | Room: 2 |
| March 4, 2003 | Location: San Diego Convention Center |

*Session Chairs:* Gerald S. Cole, Consultant USA; David Henry StJohn, University of Queensland, CAST Div. of Matls. Eng., Brisbane, QLD 4072 Australia

**8:30 AM Invited**
**Quantitative Analysis of Cast Magnesium Alloy Microstructures and their Relationships to Processing and Properties**: *Arun M. Gokhale*[1]; [1]Georgia Institute of Technology, Matls. Sci. & Eng., 771 Ferst Dr., Atlanta, GA 30332-0245 USA

Successful applications of cast magnesium alloys for structural applications require production of castings that exhibit reproducible mechanical and environmental response. Therefore, a thorough understanding of correlations between variability in the microstructure and the mechanical response, and modeling of mechanical response of the cast magnesium alloys are of interest. In this contribution, quantitative fractography and stereological techniques are applied to correlate the mechanical properties of high-pressure die-cast AZ91 and AM60 alloys with the microstructural and fractographic parameters. The data point to the control of process parameters that can reduce the variability in mechanical properties. The contribution also reports applications of the nano-indentation technique for calculation of the local constitutive behaviors of the skin and the interior regions of the cast metal through a numerical solution to the inverse problem using finite elements (FE) based simulations. The constitutive equations provide critical input to simulate micro-mechanical response of these cast microstructures.

**9:00 AM Invited**

**Solidification of Cast Magnesium Alloys**: *David Henry StJohn*[1]; Arne Kristian Dahle[1]; Trevor B. Abbott[2]; Mark Nave[3]; Ma Qian[1]; [1]University of Queensland, CAST, Matls. Eng., Sch. of Eng., Brisbane, Queensland 4072 Australia; [2]Monash University, CAST, Sch. of Physics & Matls. Eng., Melbourne, Victoria 3168 Australia; [3]Deakin University, Sch. of Eng. & Tech., Pigdons Rd., Geelong, Victoria 3217 Australia

A description of the key solidification steps in the formation of the as-cast microstructure of magnesium alloys will be presented. The focus will be on the two common magnesium alloy groups: Mg-Al alloys and Mg-Zn-rare earth alloys. The key elements to be described will be nucleation (including grain refinement), growth of the primary phase and the formation of the eutectic phases. In addition the effect of casting process (e.g. high pressure die casting, gravity die casting or sand casting) on the outcomes from solidification will be discussed. This will include consideration of the mechanisms of the formation of casting defects during solidification such as banded defects in high pressure die cast components.

**9:30 AM**

**Characterizing Solidification by Non-Equilibrium Thermal Analysis**: *Yancy W. Riddle*[1]; Makhlouf M. Makhlouf[1]; [1]Worcester Polytechnic Institute, Metal Procg. Inst., 100 Institute Rd., Worcester, MA 01609 USA

This paper presents thermal analysis data collected during the solidification of several industrially important Mg alloys. Microscope observations correlating thermal analysis with microstructure are included. These alloys are part of a larger effort at the Advanced Casting Research Center (ACRC) to catalogue the solidification behavior and resultant microstructures of established technical alloys and experimentally promising alloys. Altogether the effort is meant to aid future researchers of Mg alloys by providing a resource from which basic understanding of solidification in complicated multi-component Mg alloys may evolve. Intelligent development of new alloys with attractive mechanical properties stems from an understanding of the solidification process. Analysis of solid content accumulates as a function of both time and solidification rate, phase precipitation events, and resultant microstructures are presented for several key Mg casting alloys.

**10:00 AM Break**

**10:15 AM**

**Mechanical Properties of Investment Casting AZ91 Alloy**: *Zhan Zhang*[1]; Chantal Turcotte[1]; Guy Morin[3]; [1]Technologies Intermag, Inc., R&D, 357 rue Franquet, Sainte-Foy, Quebec G1P 4N7 Canada; [3]Centre IntÈgrÈ de Fonderie et de MÈtallurgie, 3247 rue Foucher, Trois-RiviÈres, Quebec G18 1M6 Canada

Shell mould investment casting process is able to produce thin wall and complex shape parts with good surface finish. This process is commonly applied to aluminium alloys, superalloys, steel, etc.. But its applications to magnesium alloys are limited due to mould-magnesium reactions. For enlarging the market of magnesium products, Technologies Intermag Inc. has developed technologies to prevent mould-magnesium reactions and successfully cast magnesium parts with this process. This paper presents the mechanical properties (ultimate tensile strength, yield strength, and elongation) of AZ91E magnesium alloy cast by shell mould investment casting process under as cast and after heat treatment. The results show that the mechanical properties of the test bars are much higher than those with plaster mould casting and close to those with sand mould casting. And the experiments indicate that shell investment casting process is a better alternative to sand mould casting than plaster mould casting for thin wall and complex shape parts. The effect of the cooling rate on mechanical properties of test bars will be described. The microstructure of the test bars under different conditions will be presented and the relationship between mechanical properties and microstructure will be discussed. In addition, the process for preparation of test bar shell moulds as well as the methods to prevent mould-magnesium reactions will be presented.

**10:45 AM Invited**

**Influence of Physical Data and Cooling Conditions on the Solidification in Mg-Die Castings**: *Konrad Weiss*[1]; Christoph Honsel[1]; [1]RWP GmbH, Am Muensterwald 11, Roetgen Germany

The simulation result have to fit not only in a quality way into the real foundry world. More and more the results of the simulation will be used to optimise the casting process. Here it is necessary to have a very precise knowledge of the phys. Data as well as the description of the geometry. In this paper we describe the development of physical data concerning the heat transfer during filling and solidification by different casting methods. The low pressure as well as the gravity die casting method is be used to get real data. Practical tests done under different test conditions are carried out to develop the right physical Data as well as the right conditions in the interface mould metal. The different surface conditions and the influence of the temperature of the die and the molten metal are important for the layout of the die casting process. The three different shapes where applied to different mould materials and casting methods. The cooling conditions where tested on specific items. The cooling shape was not restricted by the drilling conditions. The effect of the different cooling conditions are generated and measured. The results are the basics for the heat transfer conditions. The results are applied to real castings. The cellular phone housings are the real applications in low pressure. The use of the new conditions leads to a good process description.

**11:15 AM**

**Vacuum-Sealed Molding Process for Magnesium Casting: Numerical Simulations and Design of Experiments**: *Sayavur I. Bakhtiyarov*[1]; Ruel A. Overfelt[1]; [1]Auburn University, Mechl. Eng., 202 Ross Hall, Auburn, AL 36849-5341 USA

Given the rapid projected growth of magnesium casting usage in the automotive parts marketplace, there is a critical need to develop casting technologies applicable for a wide variety of part shapes, sizes, and production rates. The application of magnesium components will allow reductions in vehicle weight, improvement of parts-consolidation and minimizing of noise/vibration characteristics. Magnesium is considered the fastest-growing metal in cars. Many of the earliest applications are instrument panel components, valve covers, etc. These are produced by a reasonably mature die-casting technology. Many potential structural components for automobiles could be converted to magnesium if a high volume, cost effective manufacturing process were developed. In this paper we propose a modified vacuum-sealed molding process for magnesium casting. Some results of computer modeling and design of experimental research are presented.

**11:45 AM**

**Numerical Simulation of Natural Convection in Magnesium Alloy Squeeze Casting**: *Alfred Yu*[1]; *Naiyi Li*[2]; *Henry Hu*[1]; [1]University of Windsor, Mechl., Matls. & Auto., 401 Sunset Ave., Windsor, Ontario N9B 3P4 Canada; [2]Ford Motor Company, Mfg. Sys. Dept., Ford Rsrch. Lab., Rm. 2349, MD3135, 2101 Village Rd., Dearborn, MI 48124 USA

Natural convection has received less attention than conduction in metal solidification processes. It may play an important role in solidification due to its potential influence on solutes distribution in melts and grain structure. A coupled mathematical model has been developed to simulate the solidification phenomena of squeeze cast magnesium alloy (AM50). An analysis based on a Control-Volume Finite Difference approach and an Enthalpy Transforming Model was employed to understand the heat transfer and fluid flow in a cylindrical casting during solidification. The effect of natural convection on the total solidification process of squeeze casting AM50 was examined under various processing parameters, and comparison results are presented and analyzed.

## Materials Lifetime Science and Engineering - I

*Sponsored by:* Structural Materials Division, ASM International: Materials Science Critical Technology Sector, SMD-Mechanical Behavior of Materials-(Jt. ASM-MSCTS)

*Program Organizers:* Peter K. Liaw, University of Tennessee, Department of Materials Science and Engineering, Knoxville, TN 37996-2200 USA; Raymond A. Buchanan, University of Tennessee, Department of Materials Science and Engineering, Knoxville, TN 37996-2200 USA; D. Gary Harlow, Lehigh University, Mechanical Engineering and Mechanics, Bethlehem, PA 18015-3085 USA; Dwaine L. Klarstrom, Haynes International, Inc., Kokomo, IN 46904-9013 USA; Peter F. Tortorelli, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6156 USA; Robert P. Wei, Lehigh University, Mechanical Engineering and Mechanics, Bethlehem, PA 18015 USA

Tuesday AM — Room: 18
March 4, 2003 — Location: San Diego Convention Center

*Session Chairs:* Peter K. Liaw, University of Tennessee, Dept. of Matls. Sci. & Eng., Knoxville, TN 37996-2200 USA; Stephen Dale Antolovich, Washington State University, Mechl. & Matls. Eng., Pullman, WA 99164-2920 USA

**8:30 AM Invited**

**Linkage Between Safe-Life and Crack Growth Approaches for Fatigue Life Prediction**: *D. Gary Harlow*[1]; Robert P. Wei[1]; [1]Lehigh University, Mechl. Eng. & Mech., 19 Memorial Dr. W., Bethlehem, PA 18015-3085 USA

Current methods for predicting fatigue lives are based upon the safe-life and/or the crack growth approaches, both of which are empirically based. They do not adequately reflect long-term operating conditions, or identify the sources and extent of their contributions to variability. A linkage between these two approaches is established and demonstrated herein. The S-N response and its variability in fatigue life are related to key internal variables, both deterministic and random, that can be clearly identified in crack growth models. The identification and understanding of the role of these variables are paramount for predicting fatigue crack growth and subsequent damage evolution. The effectiveness of this approach is shown through analysis of an extensive set of S-N data for 2024-T4 aluminum alloy from the literature. Variability associated with manufacturing and material variables are considered. To put life prediction on sound scientific and probabilistic bases, this demonstrated linkage should be adopted.

**9:00 AM Invited**

**A Mechanistic Based Study of Fatigue Crack Propagation in the Single Crystal Nickel Base Superalloy CMSX-2**: Stephen Dale Antolovich[1]; Bruce Fergus Antolovich[2]; [1]Washington State University, Mechl. & Matls. Eng., 247 Dana Hall, Pullman, WA 99164-2920 USA; [2]Special Metals Corporation, Numeric Modlg., New Hartford, NY 13413 USA

FCP testing was done on CMSX-2 at 298 & 973K in air and vacuum for two crystallographic orientations. Two fracture surface morphologies were observed; precipitate shearing and precipitate avoidance. TEM revealed two different deformation mechanisms; precipitate shearing and bypass. A finite element analysis (FEA) was performed to predict the stresses and strains ahead of the crack tip for each tested condition. FEA, TEM and SEM observations suggest that crack growth is non-self similar and fracture surface geometry is controlled by the state of stress calling into question use of LEFM. High resolved shear stresses in the direction of the Burgers vector along with low normal stresses to the precipitates produced crystallographic crack growth while low resolved shear stresses and high normal stresses led to precipitate avoidance. This fundamental understanding of the crack growth mechanisms will assist in more accurately modelling FCP rates in single crystal Ni-base superalloys.

**9:30 AM**

**Temperature Evolution During Fatigue of HASTELLOYÆ C-2000Æ Alloy**: *Tarik A. Saleh*[1]; Bing Yang[1]; Peter K. Liaw[1]; Raymond A. Buchanan[1]; Dwaine L. Klarstrom[2]; [1]University of Tennessee-Knoxville, Dept. of Matls. Sci. & Eng., Knoxville, TN 37996-2200 USA; [2]Haynes International, Inc., 1020 W. Park Ave., PO Box 9013, Kokomo, IN 46904-9013 USA

Infrared (IR) thermography was employed as a nondestructive evaluation technique to investigate the thermal behavior of HASTELLOYÆ C-2000Æ alloy during fatigue testing. Stress-strain and S-N Curves at R ratios of 0.1 and -1 (Ûmin/Ûmax, where Ûmin and Ûmax are the applied minimum and maximum stresses, respectively) were generated for the alloy. Four stages of temperature evolution were observed: (1) an initial increase in temperature followed by a temperature decrease to (2) an equilibrium (steady-state) temperature, which held until (3) a rapid temperature increase and (4) a temperature drop after specimen failure. Additionally, the relationship between the fatigue lifetime and the steady-state temperature during fatigue testing was explored experimentally and theoretically. This research is supported by the National Science Foundation Integrative Graduate Education and Research Training (IGERT) program with Drs. W. Jennings and L. Goldberg as contract monitors, and Haynes International, Inc.

**9:50 AM**

**Elevated-Temperature Crack Growth Behavior of Nickel-Base HASTELLOYÆ X Alloy**: Y. L. Lu[1]; L. J. Chen[1]; *P. K. Liaw*[1]; G. Y. Wang[1]; S. A. Thompson[2]; J. W. Blust[2]; P. F. Browning[2]; A. K. Bhattacharya[2]; J. M. Aurrecoechea[2]; D. L. Klarstrom[3]; [1]University of Tennessee, Dept. of Matls. Sci. & Eng., Knoxville, TN 37996-2200 USA; [2]Solar Turbines, Inc., 2200 Pacific Hwy., PO Box 85376, MZ R-1, San Diego, CA 92186-5376 USA; [3]Haynes International, Inc., 1020 W. Park Ave., PO Box 9013, Kokomo, IN 46904-9013 USA

The crack-growth behavior of a nickel-base HASTELLOYÆ X superalloy was investigated under fatigue, creep, and hold-time test conditions at 816°C and 927∞C. The hold-time tests were conducted with 2-minute and 1-hour holds. It was found that the fatigue crack-growth rate could be correlated with the stress intensity factor range, DK, and the creep crack growth rate can be correlated with the stress intensity factor, K. The crack grew faster at a higher temperature. It was also noted that the introduction of a hold time at the maximum load led to an increase in the cyclic crack-propagation rate. The longer hold time gave the greater crack-growth rate. The crack-growth rates in the hold-time tests were predicted from the crack growth rates obtained from both the fatigue and the creep crack growth tests, using a semi-empirical linear summation model. Crack growth rate predictions reproduce most of the characteristics observed experimentally.

**10:10 AM**

**Development of a Generic Creep-Fatigue Life Prediction Model**: *Tarun Goswami*[1]; [1]Arkansas Tech University, Mechl. Eng., 1815 Coliseum Dr., Russellville, AR 72801 USA

Creep-fatigue life prediction of high temperature materials continues to be in the developmental stage due to the number of variables encountered and their influence in altering the cyclic lives. A generic life prediction method has been developed in this paper using the data from the following alloy groups; a) pure metals, b) solder alloys, c) copper alloys d) titanium alloys, e) low alloy steels, f) stainless steels, g) tantalum alloys and h) superalloys. Nearly 2200 data points were compiled from the published sources on the above alloy groups and independent parameters were identified within the following four test parameters, namely; 1) strain range, 2) strain rate, 3) dwell time and 4) temperature. A change in the above four parameters altered the cyclic fatigue life under the creep-fatigue conditions. Statistical Analysis Software (SAS) was used to analyze the data. The independent parameters were combined with each other up to a sixth order to produce a multivariate, best-fit, equation. The coefficient of correlation obtained in this case was 15%. Therefore, transformation functions were used in logarithmic terms and four independent parameters were evolved transforming strain rate, strain rate, dwell time and temperature, parameters. The data were analyzed with SAS and residuals were plotted for each combination of test parameters from the equation. This equation produced a coefficient of correlation of 54% and the residual plots, plotting the residuals with observed life showed a very close match in the normal probability distribution plot. These results are summarized and the generic life prediction equation presented in this paper.

**10:30 AM**

**Microstructural Simulation and Life Prediction for Advanced Gas Turbine Coatings**: *Liang Jiang*[1]; Suchismita Sanyal[1]; Sundar Amancherla[1]; Ji-Cheng Zhao[1]; Melvin R. Jackson[1]; K. Anand[1]; P. R. Subramanian[1]; Kaisheng Wu[2]; Yunzhi Wang[2]; [1]General Electric Company, One Research Cir., Niskayuna, NY 12309 USA; [2]The Ohio State University, Matls. Sci. & Eng., 2041 College Rd., Columbus, OH 43210 USA

In the severe operation environment of gas turbines, advanced metallic coatings are used as environmental coatings or as bond coats between superalloy substrate and ceramic thermal barrier coating for protecting substrate superalloy from oxidation and hot corrosion. Both oxidation and interdiffusion between the metallic coatings and substrate alloys result in complex and progressive degradation of the metallic coating, especially the reduction of aluminum concentration in the coating. Coupled with thermodynamic and kinetic databases, a simplified model with consideration of Ni-Cr-Al multicomponent diffusion in single phase was developed for the calculation of interdiffusion profiles and lifing of metallic coatings. A more sophisticated model with consideration of Ni-Cr-Al multicomponent diffusion in multiphase was developed for the microstructural evolution in coatings. The models †help understand the failure mechanisms of metallic coatings for gas turbines and can capture the detrimental effects resulting from oxidation and interdiffusion.

**10:50 AM**

**Effect of the Microstructure on the Very High Cycle Fatigue of Titanium Alloys at Room and Cryogenic Temperatures**: *Claude Bathias*[1]; [1]CNAM/ITMA, 2 rue ContÈ, Paris 75003 France

In several industries, the required design lifetime of many components often exceeds 10^8 cycles. This requirement is applicable to aircraft turbine but also for space engine such as cryogenic pump. Although a large amount of fatigue data has been published in the form of S-N curves, the data in the literature have been limited to 10^7 cycles. Time and cost constraints rule out the use of conventional fatigue tests of more 10^7 cycles to check structural materials. A possibility of accelerated testing of specimens is now considered by using a piezoelectric fatigue machine working at high frequency. A short description of the machine is given. It is found that there is no asymptote after 10^7 cycles and that the SN curve is always decreasing up to 10*9 cycles for TA4V6 or 6246 Ti alloy at room and at cryogenic temperature. The effect of forging process is very important in the gigacycle fatigue, inducing sometime a shift of more than 100 MPa between the SN curves. After 10^7 cycles the initiation mechanism is always at the interior of the specimen and related to the size of the alpha platelets. The mechanism is discussed. A special device has been built in our laboratory in order to test specimens in liquid hydrogen, and to determine the S-N curve up to 10^8 cycles. A short description of the device is given. A comparison between those results and data in gas helium is made and discussed. It is confirmed that the fatigue strength at 20 Kelvin is much higher than at room temperature, but affected by hydrogen or helium.

**11:10 AM Invited**

**Contact Fatigue of Dental Multilayers**: *M. Huang*[1]; X. Niu[1]; Z. Suo[1]; V. Thompson[2]; D. Rekow[2]; W. O. Soboyejo[1]; [1]Princeton University, Princeton Matls. Inst. & Dept. of Mechl. & Aeros. Eng., Princeton, NJ 08544 USA; [2]New York University, Coll. of Dentistry, New York, NY 10034 USA

This paper presents the results of a combined experimental and computational study of contact fatigue in multilayered structures that are relevant to dental restorations. These include top layers of crown materials (zirconia, alumina and Empress II) that are bonded to dentin or materials with equivalent elastic properties to dentin. Cyclic contact-induced deformation is shown to result in viscoelastic/viscoplastic deformation and ratcheting phenomena that give rise ultimately to sub-surface pop-in. The local conditions for pop-in are also determined from hydraulic fracture experiments that utilize fluid pressure in the loading of cracks/notches within dental materials. The measured pop-in conditions are then used as critical conditions in finite element models of the effects of viscous flow on the pressure loading within cracks/notches. Finally, the physical insights and finite element models are integrated into a mechanism-based framework for the prediction of fatigue damage in multilayered structures that are relevant to dental restorations.

**11:40 AM Invited**

**Physically-Based Models for the Prediction of Fatigue and Dwell Fatigue Crack Growth in Ti-6242: Comparison of Models with Experiments**: F. McBagonluri[2]; Chris Mercer[1]; E. Akpan[1]; W. Shen[1]; *W. O. Soboyejo*[1]; [1]Princeton University, Princeton Matls. Inst., D404 E. Quad., Princeton, NJ 08544 USA; [2]University of Dayton, Dept. of Matls. Eng., Dayton, OH 45390 USA

This paper presents the results of a combined experimental and theoretical/computational study of fatigue and dwell fatigue crack growth in Ti-6242 with three different microstructures (equiaxed, elongated and colony a/b structures). The micromechanisms of short and long fatigue growth are studied using interrupted fatigue tests and beachmarking techniques. The insights developed during these experiments are then used to guide the development of physically-based fracture mechanics models for the prediction of crack growth during fatigue or dwell fatigue loading. The predictions from the models are compared with experimental measurements of sub-surface and surface crack growth. The implications of the results are then discussed for the modeling of fatigue and dwell fatigue in engineering structures and components.

## Materials Processing Fundamentals: Powder Synthesis and Processing

*Sponsored by:* Extraction & Processing Division, Materials Processing & Manufacturing Division, Jt. MPMD/EPD-Process Modeling Analysis & Control Committee, EPD-Process Fundamentals Committee

*Program Organizers:* Adam C. Powell, Massachusetts Institute of Technology, Department of Materials Science and Engineering, Cambridge, MA 02139-4307 USA; Princewill N. Anyalebechi, Grand Valley State University, L. V. Eberhard Center, Grand Rapids, MI 49504-6495 USA

Tuesday AM — Room: 1A
March 4, 2003 — Location: San Diego Convention Center

*Session Chair:* Princewill N. Anyalebechi, Grand Valley State University, L. V. Eberhard Center, Grand Rapids, MI 49504-6495 USA

**8:30 AM**

**Extremely Rapid Sintering of Bronzes,Steels and Refractory Metals (W, Re) and Hard Metals (WC, Tin, Tib2, Etc.) In2.45 Ghz Multi- and Single- Mode Microwave Fields**: Dinesh Agr[1]; Jiping Cheng[1]; Rustum Roy[1]; *A. Upadhyay*[1]; [1]The Pennsylvania State University, Matls. Rsrch. Inst., University Park, PA 16802 USA

To the surprise of nearly everyone including the authors, it has been shown that all common metal powders can be sintered routinely in common microwave (2.45, 0.915 GHz) apparatus in 10-30 minutes. The sintering times for all are reduced by more than one order of magnitude. Pre-alloying mixtures react even faster than alloyed powders. Continuous compositional gradation from steels to ìhard metalsî are easily achieved. Magnetic metals display unexpected behaviors in H fields. Microstructure differences (SEM level) will be used to suggest that the nature of the porosity may provide the explanation for some of the improved properties. In two-phase systems the unique ìanisothermalî conditions attained in a microwave field also play a major role.

**9:00 AM**

**Processing Ti3Al/Al2O3 Composites Using Mechanical Milling**: *Gorgees Adam*[1]; [1]University of Waikato, Waikato Ctr. for Adv. Matls., PB 3105, Hamilton 2001 New Zealand

A Ti3Al(O)/Al2O3 metal matrix composite material was produced by sintering an Al/TiO2 composite powder produced using high mechanical milling. The composite typically contains 50-60vol.%Al2O3. We have recently developed a low cost process which allows us to reduce (or increase) the volume fraction of the Al2O3 phase in the composite material. This process involves the use of several physical and chemical separation techniques. The detailed process itself is confidential at the time of writing this abstract, and a provisional patent application has been filed. By using this process, we have successfully reduced the volume fraction of the Al2O3 phase in the Ti3Al/Al2O3 composite from 50-60% to 20-30%. This favourable outcome shows that the process facilitates the freedom of controlling the volume fraction of the Al2O3 particles in the composite to achieve a variety of different mechanical properties desirable for different applications. This paper will introduce and discuss this process and the mechanical properties of the composites produced.

**9:20 AM**

**Effect of Surface Oxidation on the Sintering Activity of Al Powders**: *Fei Tang*[1]; Stacy Scott[1]; Fran Laabs[1]; Iver Eric Anderson[1]; [1]Iowa State University, Ames Lab., Metal & Ceram. Scis. Prog., Rm. 223, Metals Dvlp. Bldg., Ames, IA 50011 USA

In order to promote the sintering behavior and eventually improve the performance of Al parts made by powder metallurgy, very high purity Al powders (99.99%) with a thin, passive surface oxide were produced by a gas atomization reaction synthesis (GARS) technique. Vacuum sintering at 525°C for 24, 48, 72 and 100 h of fine (dia.<10µm), tap densified commercial purity (CP) and GARS Al powders produced extensive necking in the GARS samples, but essentially no detectable sintering in the CP samples. BET measurements of the surface area of both kinds of Al samples at 500, 525, and 550°C quantified the relative sintering kinetics. The enhancement of GARS Al sintering activity may be attributed to the very thin oxide (3-5nm) layer on the GARS powder compared with the 10-20nm oxide layer on the CP Al powder. Funding of this project is from DOE Basic Energy Sciences under contract number W-7405-Eng-82.

**9:40 AM**

**Inductively Coupled Plasma Deposition of Ceramic Thin Films: A Review**: Patrick R. Taylor[1]; *Edgar E. Vidal*[1]; [1]Colorado School of Mines, Metallurgl. & Matls. Eng., 1500 Illinois St., Hill Hall, Golden, CO 80401-1887 USA

The deposition of ceramic materials onto substrates has always been of special interest in the development of surface related technologies. Special interest has been placed on using thermal plasma as the deposition method, specifically inductively coupled plasmas. Many different modifications to the same basic principle of deposition have been performed through out the materials research community. Such technique has many advantages over more conventional techniques, such as high deposition rates, high surface area coverage, clean energy source, no contamination from electrodes and near atmospheric pressures. Materials deposited vary from simple oxide systems like TiO2 to more complex structures like ternary oxides and nitrides. This paper reviews recent developments relative to the inductively coupled plasma deposition of thin films.

**10:00 AM Break**

**10:20 AM**

**Analysis of Gas Atomization Process Physics**: *Iver Eric Anderson*[1]; Robert Lee Terpstra[1]; Sebastian Rau[2]; Boris Rauscher[2]; Richard S. Figliola[3]; [1]Iowa State University, Ames Lab. (USDOE), 222 Metals Dvlp. Bldg., Ames, IA 50011 USA; [2]University of Bremen, Bremen

TUESDAY AM

28331 Germany; [3]Clemson University, Dept. of Mechl. Eng., Clemson, SC 29631 USA

The development of a discrete jet, close-coupled gas atomization nozzle which operates over a wide pressure range in an open wake condition has enabled the study of the effect of gas velocity, from Mach 2.5 to 3.5, on the size distribution of the resulting powder. Achievement of a sufficiently narrow geometric standard deviation, 1.95 or less, of the powder size results permitted a meaningful comparison with the mean size predictions of two atomization models based on capillary and acceleration wave formation. High-speed cinematography permitted observation of near-field (primary) and downstream (secondary) melt break-up processes. Correlations with gas-only measurements and schlieren imaging detected changes in wake recirculation related to melt stream splitting as a function of atomization gas pressure (for N2 and Ar) and nozzle design. Analysis of these results suggests further work to increase understanding of this complex process. Support by USDOE-BES and the Process Science Initiative under contract no. W-7405-Eng-82.

**10:40 AM**

**Barium-Strontium Titanate Powder Synthesis in a Thermal Plasma Reactor**: Patrick R. Taylor[1]; *Edgar E. Vidal*[1]; Ana M. Vera-Arcetti[2]; [1]Colorado School of Mines, Dept. of Metallurgl. & Matls. Eng., 1500 Illinois St., Hill Hall, Golden, CO 80401-1887 USA; [2]Indinvest, S.p.A. , Production Dept., Biassono, Milan Italy

The synthesis of high-purity ultra-fine barium strontium titanate powders (BST: $Ba_{0.6}Sr_{0.4}TiO_3$) has been performed in a non-transferred arc D.C. thermal plasma reactor. Slurries of barium and strontium nitrates and titanium dioxide were used as precursors. Oxygen and argon were used as carrier gas, and pure argon and combinations of argon and nitrogen were used as plasma gases. The plasma torch power was varied, as well as the oxygen flow rate and the total molar concentration of the precursors. A graphite plate was designed to protect the torch electrode and lower the level of impurities in the product. The powders collected from the different sections of the reactor were characterized using Transmission and Scanning Electron Microscopy, X-Ray Diffraction, and chemical analysis. The powders produced showed total conversion to BST, ultra-fine particle size (< 30 nm) and high purity, which makes this a potential ceramic material for electronic devices.

**11:00 AM**

**Preparation of Acicular Nickel Powder by a Modified Polyol Process**: *Hun S. Chung*[1]; Dong J. Kim[1]; Kening Yu[2]; [1]Korea Institute of Geoscience and Mineral Resources, Minls. & Matls. Procg., 30 Kajung-dong, Yoosung-ku, Daejeon 305-350 Korea; [2]Chinese Academy of Sciences, Inst. of Process Eng., PO Box 353, Beijing 100080 China

Morphology of fine metal powders becomes important depending on their industrial applications. In the present study, a combined process of chemical reduction and polyol processes was attempted to prepare acicular nickel powders. Experiments were carried out under the various conditions of reactant concentration, reduction time, and reaction temperature. The nickel powders of 1~10 micrometers in length and 0.1~0.6 micrometers in diameter were synthesized with nickel hydrooxide slurry in ethylene glycol which was obtained from nickel sulfate and sodium hydroxide, and hydrazine hydrate was used as a reducing agent. The reduction was completed within 60 minutes at the temperature of 80 to 95 Celsius, and the produced powder was finely dispersed without agglomeration.

**11:20 AM**

**The Mechanical Properties of Al Foam by Batch Process**: *Bo Young Hur*[1]; *Sang Youl Kim*[1]; *Soo Han Park*[1]; *Duck Kyu Ahn*[1]; *Chol Kyu Kwon*[1]; [1]Gyeongsang National University, ULSFoM-NRL, ReCAPT, Div. of Matl. Eng., 900, Kajoa-Dong, Chinju 660-701 S. Korea

Metallic foam which has light-weight and thermal resistance structure was expected synergy effect on mechanical, thermal absorption properness from energy and environmental problem it was composed of solid and pore as composite material was controlled of pore shaper, cell size, cell size distribution and porosity by manufacturing process. Porous Aluminum was manufactured by down pot stirring furnace with used Aluminum alloy. The measurement of porosity were calculated by image microscope, and so. The uniaxial compression test was performed with a universal testing machine. The Compressive stress-strain curve of cellular solids can be divided into three regions: the linear elastic, the plateau, and the densification. The absorption energy per unit volume of Al foam was evaluated. The absorption energy can be evaluated by integrating the area under the stress-strain curve. The average value of absorption energy per unit volume of Al foam at a strain of 50% is 3MJ/m3.

**11:40 AM**

**Effects of Heat Treatment on Foam Struts and their Measurement**: *Jikou Zhou*[1]; [1]Princeton University, Dept. of Mechl. & Aeros. Eng., Princeton, NJ 08544 USA

This paper examines the effects of heat treatment on open-cell aluminum foam struts. First, the strut microstructures are characterized via SEM, FIB and TEM. The stress-strain behaviors of struts extracted from the as-received and aged foams are determined using micro-tensile testing techniques. The strut microstructures and mechanical properties are then compared with those of the bulk materials from which the foams are fabricated. Finally, the effects of heat treatment of foam struts are discussed.

## Materials Processing Under the Influence of Electrical and Magnetic Fields - III

*Sponsored by:* Extraction & Processing Division, Materials Processing & Manufacturing Division, EPD-Process Fundamentals Committee, Jt. MPMD/EPD-Process Modeling Analysis & Control Committee

*Program Organizers:* Joanna R. Groza, University of California-Davis, Chemical Engineering Material Science Department, Davis, CA 95616 USA; George S. Dulikravich, The University of Texas at Arlington, Multidisciplinary Analysis, Inverse Design, and Optimization (MAIDO) Program, Department of Mechanical and Aerospace Engineering, Arlington, TX 76019 USA; Nagy H. El-Kaddah, University of Alabama, Department of Metallurgical & Materials Engineering, Tuscaloosa, AL 35487-0202 USA; James W. Evans, University of California, Department of Materials Science and Mineral Engineering, Berkeley, CA 94720 USA; Zuhair Munir, University of California, College of Engineering, Davis, CA 95616-5294 USA; Srinath Viswanathan, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6083 USA

Tuesday AM — Room: 14A
March 4, 2003 — Location: San Diego Convention Center

*Session Chair:* George S. Dulikravich, University of Texas at Arlington, Dept. of Mech. & Aero. Eng. Dept. MAIDO Prog., Arlington, TX 76019 USA

**8:30 AM Opening Remarks**

**8:35 AM**

**Fluid Flow Motion and Solidification Under Combined Action of Magnetic Fields and Microgravity**: *Ben Q. Li*[1]; Kai Li[1]; Yan Shu[1]; Henry C. de Groh[2]; [1]Washington State University, Sch. of Mechl. & Matls. Eng., Pullman, WA 99164 USA; [2]NASA Glenn Center, Cleveland, OH 44135 USA

Mathematical models are developed to represent g-jitter induced fluid flows and their effects on solidification under combined action of magnetic fields and microgravity. The numerical model development is based on the finite element solution of governing equations describing the g-jitter driven fluid flows, heat transfer and solutal transport with and without an applied magnetic field in space vehicles. The numerical model is applied to study an upcoming shuttle flight experiment system that involves the growth of crystals from melts. To validate the model predictions, an g-jitter simulator is developed using the oscillating wall temperatures where timely oscillating fluid flows are measured using a laser PIV system. The measurements are compared well with computed results.

**8:55 AM Invited**

**Using the Magnetic Body Force to Eliminate g-Jitter in Microgravity Experiments**: C. D. Seybert[2]; *James W. Evans*[1]; [1]University of California-Berkeley, Matls. Sci. & Eng., Berkeley, CA 94720 USA

Although orbiting laboratories provide environments which can minimize density-based convection, residual accelerations, or g-jitter, still exist. This complicates experiments, for example on solidification at the diffusional limit. Low-frequency or steady (ìDCî) accelerations are difficult or impossible to eliminate by damping. This paper details the use of magnetic fields to counter these accelerations. Using accelerometers and a three-axis magnet system, residual acceleration could be effectively eliminated. Absolute control of the conditions during, say, crystal growth could be achieved. We have designed a magnet with a uniform magnetic field gradient for possible use in space experiments. Modeling of the flow induced by random accelerations will be presented, along with comparisons to the flow when the g-jitter is countered by the magnet system.

**9:25 AM Invited**
**Optimization of Intensities and Orientations of Magnets Controlling Melt Flow During Solidification**: *Brian H. Dennis*[1]; George S. Dulikravich[2]; Marcelo Colaco[2]; [1]University of Tokyo, Grad. Sch. of Frontier Sci., 7-3-1 Hongo, Bunko-ku, Inst. of Environml. Studies, Tokyo 113-8656 Japan; [2]University of Texas at Arlington, Mech. & Aeros. Eng. Dept., Multidisciplinary Analy., Inverse Design & Optimization (MAIDO) Prog., UTA Box 19018, Arlington, TX 76019 USA

When growing a large single crystal, such as a semiconductor crystal, it is desirable to remove the thermally induced convection effects entirely, leading to heat transfer by pure conduction. If the melt speed is low, it is less likely that small particles of the crucible wall will be deposited in the mushy region and consequently in the crystal. It is also desirable to achieve a distribution of the dopant in the crystal that is as uniform as possible. A least-squares spectral finite element method was used to develop an accurate computer code for prediction of solidification from a melt under the influence of an externally applied magnetic field. A micro-genetic optimizer was used with this solidification analysis to determine the distributions of the magnets and the shape of the crucible that will minimize the convective flow throughout the melt or in desired regions of the melt only.

**9:55 AM Break**

**10:10 AM**
**Melt Flow Instability and Turbulence in Electromagnetically Levitated Droplets**: Xin Ai[1]; *Ben Q. Li*[1]; [1]Washington State University, Sch. of Mechl. & Matls. Eng., Pullman, WA 99164 USA

Magnetically levitated droplets have found a wide range of applications in both industrial and materials processing in microgravity environment. One of the critical issues concerning the applications of these droplets is the internal melt flows induced by the applied electromagnetic fields. This paper addresses these issues through the numerical analysis of fluid flow instabilities and flow transition to turbulence chaotic motions and direct numerical simulations of turbulence in magnetically levitated droplets. Numerical implementation and computed results are presented for flow instability and turbulence flows in magnetically levitated droplets under terrestrial and micro gravity conditions.

**10:30 AM**
**A Contactless Inductive Velocity Reconstruction Method for Metallic and Semiconducting Melts**: *Frank Stefani*[1]; Gunter Gerbeth[1]; [1]Forschungszentrum Rossendorf, MHD Dept., PO Box 510119, Dresden D-01314 Germany

The knowledge of the flow in metallic and semiconducting melts is important for a number of industrial problems. Optical methods cannot be applied due to the opaqueness of those fluids. Ultrasonic methods have problems with wetting and thermal stability when applied in hot metallic melts. Evidently, contactless methods for velocity determination would be highly desirable. In some applications even a coarse knowledge of the flow topology and the direction of the main eddies would be of high value. We study the possibility of velocity reconstruction in electrically conducting fluids from external measurements of different induced magnetic fields. It is shown that for a reliable velocity reconstruction the effect of the electric potential at the fluid boundary on the induced magnetic field should be taken into account.

**11:00 AM**
**Fluid Velocity Measurements in Electro-Vortical Flows**: *A. Cramer*[1]; P. Terhoeven[2]; A. Kraetzschmar[2]; G. Gerbeth[1]; [1]Forschungszentrum Rossendorf, MHD Dept., PO Box 510119, Dresden D-01314 Germany; [2]Moeller, Ltd., Hein-Moeller-Str. 7-11, Bonn D-53115 Germany

This class of flows is characterized by the feeding of strong electrical currents into a volume of liquid metal. The interaction of these currents with their own magnetic field drives flows which exhibit phenomena like formation of jets and pinch-effect. Further increasing the current may lead to disruption of the melt column accompanied with a discharge. This can be used for a liquid metal current limiter with self-healing properties. The paper will give results from a systematic study of the flow structure performed by means of our mechano-optical velocity probe. The measurements have been done in a liquid metal column carrying an axial current of several 100 Amps. The column was separated by an insulating plate with a small hole drilled in the center thus restricting the current path. The measured flow structure of the evolving jet was found to be in good agreement with our numerical simulation.

**11:20 AM**
**Droplet Deformation and 2-D/3-D Marangoni Flow Phenomena in Electric Fields**: Yunlong Huo[1]; *Ben Q. Li*[1]; Song Suping[2]; [1]Washington State University, Sch. of Mechl. & Matls. Eng., Sloan 207, Pullman, WA 99164 USA; [1]Washington State University, Sch. of Mechl. & Matls. Eng., Pullman, WA 99164 USA; [2]Washington State University, Sch. of Mechl. & Matls. Eng., Pullman, WA 99164 USA

An integrated numerical model is presented for free surface phenomena and Marangoni fluid flows in electrically levitated droplets under both terrestrial and microgravity conditions. The model development is based on the boundary element solution of the Maxwell equations simplified for electrostatic levitation applications and the free surface deformation that is primarily caused from the surface Maxwell stresses resulting from the applied electric fields. The electric and free surface model is further integrated with a finite element model for the surface tension induced fluid flows in the levitated droplets. Both 2-D and 3-D fluid flow structures may be developed in the electrically levitated droplets depending on the applied laser heating sources. The integrated model is applied to study the electric field distribution, free surface deformation and 2-D and 3-D (both transient and steady state) internal fluid flow structures in normal and micro gravity for both symmetric and tetrahedral heating arrangement.

**11:40 AM**
**Natural Convection of Liquid Gallium Under a Magnetic Field with Application of Electric Current**: *Masayuki Kaneda*[1]; Toshio Tagawa[1]; Hiroyuki Ozoe[1]; [1]Kyushu University, IAMS, 6-1 Kasuga Koen, Kasuga, Fukuoka 816-8580 Japan

The heat transfer rate of natural convection of liquid gallium in a cubic enclosure was measured under the influence of magnetic field with or without external electric current applied from outside. The one vertical wall of the enclosure was heated with constant heat flux and an opposing wall was cooled isothermally by electro-conductive walls and four other walls were thermally and electrically insulated. Magnetic field horizontal and parallel to the hot and cold walls was applied. Electrodes were placed at the center of both hot and cold walls and electric current flows from the cold wall to the hot wall, which presumes the thermoelectric current. Resulted Nusselt number on the hot wall decreased by applying a magnetic field only, but both magnetic field and electric current change the average Nusselt number. Combination of magnetic filed and electric current may control the natural convection by induced Lorentz force.



## Materials Prognosis: Integrating Damage-State Awareness and Mechanism-Based Prediction: Global & Local Interrogation

*Sponsored by:* Structural Materials Division,
*Program Organizers:* James M. Larsen, US Air Force, Air Force Research Laboratory, Materials and Manufacturing Directorate, Wright-Patterson AFB, OH 45433-7817 USA; Leo Christodoulou, Defense Advanced Research Agency, Arlington, VA 22203-1714 USA; William J. Hardman, Naval Air Systems Command, Propulsion and Power Directorate (AIR 4.4.2), Patuxent River, MD 20670-1534 USA; Andrew J. Hess, Naval Air Systems Command, Propulsion and Power Directorate, Patuxent River, MD 20670-1534 USA; J. Wayne Jones, University of Michigan, College of Engineering, Department of Materials, Science and Engineering, Ann Arbor, MI 48109 USA; Stephan M. Russ, Air Force Research Laboratory, Materials and Manufacturing Directorate, AFRL/MLLN, Wright-Patterson Air Force Base, OH 45433-7817 USA

Tuesday AM — Room: 16A
March 4, 2003 — Location: San Diego Convention Center

*Session Chairs:* Stephan M. Russ, Air Force Research Laboratory, Matls. & Mfg. Direct., WPAFB, OH 45433-7817 USA; Michael L. Dent, Air Force Research Laboratory - Anteon Corp., Matls. & Mfg. Direct., WPAFB, OH 45433-7817 USA

**8:30 AM Invited**
**Overview of Technologies to Support Risk-Based Prognostic Decision System**: *Thomas A. Cruse*[1]; [1]Consultant, 398 Shadow Pl., Pagosa Springs, CO 81147 USA

The presentation covers a recently-completed AF-sponsored study to explore and assess technologies that could be used to support a risk-based decision for continued flight operations of individual legacy turbine engines. The focus of the study was to reduce the uncertainties in the prognostic evaluation of remaining life through innovative material state sensing and new thermal history recording sensors. The decision system is based on a Bayesian network life model and a predictive confidence interval strategy tied to the quality of the input data. Material state modeling is the most urgent need given that the material is the source of greatest uncertainty in making a risk-based decision for continued operations. The presentation will discuss each element of the proposed decision system while emphasizing the required innovations for state awareness, microstructural modeling, and network modeling that must be addressed in future prognostic systems.

**9:00 AM Invited**

**Enhanced Prognosis Through Probabilistic Damage Assessment**: *Stephen J. Hudak*[1]; Michael P. Enright[1]; Harry R. Millwater[2]; R. Craig McClung[1]; [1]Southwest Research Institute, Matls. Eng. Dept., 6220 Culebra Rd., San Antonio, TX 78238-5166 USA; [2]University of Texas at San Antonio, San Antonio, TX 78249 USA

This paper examines the potential benefits of integrating fully probabilistic life prediction methods into the prognostics process. This was accomplished by using an existing probabilistic life predictions code (DARWIN) as a demonstration platform. DARWIN was modified to accept actual aircraft engine (F-16/F100) data from flight data recorders. Modules were also added to DARWIN to transform engine speed (RPMs) to stress, filter the stress to enhance computational efficiency, add crack initiation (to the existing crack propagation capability), and expand the frequency of inspection capability to simulate continuous onboard monitoring. Example analyses were performed for fatigue critical locations on a generic bladed compressor disc. Extensive usage data were analyzed and used to characterize the influence of inter- and intra-mission usage variability on disk fatigue life and probability of failure. Analyses were also performed to demonstrate the significant reliability benefits of continuously monitoring damage with onboard sensors, even when detection sensitivities are appreciably less than those commonly employed in depot inspections.

**9:25 AM Invited**

**Damage Indicators for Advanced Life Prediction Systems**: *Eva L. Suarez*[1]; Yoshika Omori[1]; Michael J. Duffy[1]; [1]Pratt & Whitney, Fatigue & Fracture Mech., 400 Main St., MS 163-07, E. Hartford, CT 06108 USA

New techniques for tracking engine component life usage have been devised to improve current engine life tracking processes, providing the customer with a safer, more reliable, affordable, and comprehensive damage prognosis tool. The new technique consists of damage accumulated at real time by quantitative algorithms, relating aircraft and engine gas path continuously measured or calculated performance data to the assessment of total remaining capability for the engine componentís critical life limiting locations. Two methodologies have been developed, evaluated, and compared against its classical life-tracking counterpart. One is a statistical approach where the uncertainty is evaluated by levels of confidence on the results. The second is a first principle physical relation governing damage mechanisms and the outcome was compared to Finite Element Methods thermal and structural results. Material behavior algorithms have been developed for various failure modes. Life indicator prediction results have shown very high correlation to design analysis as indicated by the high statistical coefficients of determination.

**9:50 AM Break**

**10:20 AM Invited**

**eSTORM: Enhanced Self Tuning On-Board Real-Time Engine Model**: *Thomas Brotherton*[1]; Al Volponi[2]; Rob Luppold[3]; Donald L. Simon[4]; [1]Intelligent Automation Corporation, 13029 Danielson St., Ste. 200, Poway, CA 92064 USA; [2]Pratt & Whitney, E. Hartford, CT 06108 USA; [3]Luppold & Associates, 164 N. Water St., W. Newton, PA 15089 USA; [4]US Army Research Laboratory, NASA Glenn, Cleveland, OH 44135 USA

A key to producing reliable engine diagnostics resides in the fusion of processing algorithms. Fusion of techniques has been shown to improve diagnostic performance while simultaneously reducing false alarms. Presented here is an approach that fuses a physical model called STORM (Self Tuning On-board, Real-time engine Model), with an empirical neural net model to provide a unique hybrid model called enhanced STORM (eSTORM) for engine diagnostics. STORM is a piecewise linear approximation of the engine cycle Deck. STORM provides significant improvement over existing real-time engine model methods however, there are several effects that impact engine performance that STORM does not capture. Integrating an empirical model with STORM accommodates the modeling errors. This paper describes the development of eSTORM for a Pratt & Whitney F117 turbofan engine. Comparative results of using STORM and eSTORM on simulated engine data are presented. eSTORM is shown to work extremely well in reducing STORM modeling errors and biases for the conditions considered.

**10:45 AM Invited**

**Vibration-Based Crack Detection in Rotating Engine Components**: *HÈctor M. RodrÌguez*[1]; Huageng Luo[1]; Dennis M. Corbly[2]; [1]GE, Global Rsrch., 1 Research Cir., K1-2A72, Niskayuna, NY 12309 USA; [2]GE, Aircraft Engines, 1 Neumann Way, A413, Cincinnati, OH 45215 USA

A physics-based approach for the detection of cracks in rotating disks is presented. The approach takes advantage of the distinct behavior in the vibration response of cracked rotating disks. In particular, radial-axial cracks induce a unique vibration response as they open due to tensile hoop stresses caused by centrifugal loading. The crack opening forces a redistribution of the disk mass. This mass redistribution yields an additional unbalance that is proportional to the square value of the speed, and hence the resulting crack-induced unbalance force is proportional to the fourth power of the speed. This unique unbalance response characteristic brings the opportunity to implement a monitoring system to detect early stage disk cracks by measuring the vibration response of the rotating assembly at non-invasive locations (e.g., bearings). The present work shows an experimental study of the proposed crack detection approach. In the test, an aircraft engine disk in a spin pit is used to investigate the change in the rotor vibration response during the growth of an induced crack in a highly stressed location. The results from the test provide a further insight into the technique and its potential implementation as a prognostic tool for engine health management.

**11:10 AM Invited**

**USN Rotor Spin Facility Experience with Disk Crack Detection Sensing Technology**: *Greg C. Muschlitz*[1]; [1]NAVAIR, AIR 4.4.7.1, B106, Unit 4, 22195 Elmer Rd., Patuxent River, MD 20670-1534 USA

The US Navy has been actively pursuing and developing advanced disk crack detection sensing systems from various vendors. The Rotor Spin Facility has been actively testing these systems to determine maturity and capability of these systems. Spin testing capability will be discussed including the results of several disk crack detection efforts recently concluded. Future plans will also be discussed.

**11:35 AM Invited**

**Updating Turbomachinery Fatigue Life Remaining by Use of Blade-Tip Sensors**: *Andreas H. von Flotow*[1]; [1]Hood Technology Corporation, 1750 Country Club Rd., Hood River, OR 97031 USA

Blade tip sensors in turbomachinery can monitor aspects of the stress state of blades and can detect accumulating damage of blades and their host disks. A system employing these sensors can operate continuously, whenever the machine operates. The challenge is to develop techniques for using this information for prognosis. Current practice for quantifying fatigue life of rotating components of turbomachinery specifies life in units of operating time, or ìequivalent engine cycles.î No account is taken of the operating conditons. Nor is an attempt made to detect and track damage accumulating during operation. The new capability with blade-tip sensors promises to deliver improvements over this current operating procedure. This presentation will outline the prognostics capabilites promised by use of blade tip sensors, showing data from seeded fault tests. The presentation will outline the prognostics techniques in development. Finally, the presentation will illuminate the need for tighter linkage between this development work and existing expertise in fatigue life quantification.

## Measurement and Interpretation of Internal/ Residual Stresses: Welding

*Sponsored by:* Structural Materials Division, ASM International: Materials Science Critical Technology Sector, Materials Processing & Manufacturing Division, SMD-Mechanical Behavior of Materials-(Jt. ASM-MSCTS), MPMD-Shaping and Forming Committee

*Program Organizers:* Craig S. Hartley, Air Force Office of Scientific Research, Arlington, VA 22203 USA; Mark A.M. Bourke, Los Alamos National Laboratory, Neutron Science Center, Los Alamos, NM 87545 USA; Bimal K. Kad, University of California, Ames Laboratory, La Jolla, CA 92093-0085 USA

Tuesday AM  Room: 17B
March 4, 2003  Location: San Diego Convention Center

*Session Chairs:* Craig S. Hartley, Air Force Office of Scientific Research, Arlington, VA 22203 USA; Thomas Gnaupel-Herold, NIST Center for Neutron Research, Gaithersburg, MD 20899-8562 USA

**8:30 AM Invited**
**Application of X-Ray and Neutron Residual Stress Mapping to Understand Cracking of Kraft Recovery Boiler Tubes and Air Ports**: *Camden R. Hubbard*[1]; James R. Keiser[1]; Gorti B. Sarma[1]; Kimberly A. Choudhury[1]; [1]Oak Ridge National Laboratory, Metals & Ceram. Div., MS 6064, Bldg. 4515, Oak Ridge, TN 37830-6064 USA

Cracking of 304L stainless steel/carbon steel co-extruded tubes that form floors and walls in most recovery boilers is being observed with increasing frequency in North American boilers. The relationship among stresses in the floor, wall tubes and air port tubes to operating conditions and crack advance into the carbon steel is being investigated. Both X-ray and neutron diffraction and finite element modeling are being used to characterize the surface and through thickness residual stresses throughout boiler operation. The measured residual stresses have been used both as initial conditions for finite element models and for improving and validating the models. Other studies have evaluated the cracking resistance of several alloys that are alternatives to the conventionally used 304L stainless steel. Understanding of the air port forming process and design is underway to see if alternate materials and alternate forming methods can reduce the probability of cracking.

**9:00 AM Invited**
**Phase-Resolved Residual Stresses Around a Weld in the Single Crystal Superalloy CMSX-4**: *David Dye*[1]; Ronald B. Rogge[1]; Kelly T. Conlon[1]; Roger C. Reed[2]; [1]National Research Council of Canada, Neutron Prog. for Matls. Rsrch., Chalk River Labs., Chalk River, Ontario K0J 1J0 Canada; [2]University of British Columbia, Dept. Matls. & Metals Eng., 309-6350 Stores Rd., Vancouver, BC V6T 1Z4 Canada

The repair welding of single crystal nickel-base Superalloy gas turbine blades is of great interest because it allows remediation of defects in large castings that would otherwise be scrapped. Sealing welds and blade tip repair are also being explored. Measurement of the full residual stress tensor in both the gamma and gamma-prime phases around an autogenous weld in a coupon of CMSX-4 is demonstrated, with rationalization of the results using a finite element model of the welding process. The measurements were performed using constant-wavelength neutron diffraction, and demonstrate that in the weld and heat-affected zone the principal tensile residual stress is in the radial direction, that the hoop stresses are compressive and that the shear stresses appear to be small. Cracking, when it occurs, occurs on {110}-type planes. Finally, the weld region appears to retain the orientation of the parent material.

**9:30 AM**
**Neutron Diffraction Residual Stress Measurements on Single Crystal Superalloy Weld Joints**: Ganjiang Feng[1]; [1]GE, 1 River Rd., 55-127, Schenectady, NY 12345 USA

Single crystal nickel-base superalloys are widely used in aircraft and advanced industry gas turbine components, which are often made by investment casting and exposed to high temperatures and cyclic loadings over extended periods of time. Due to the complexity of the turbine components, it is inevitable to employ joining processes during fabrication and repair. However, the single crystal alloys containing greater than 10% refractory elements are generally viewed as unweldable. Due to the high strength and the strong precipitation reaction of the single crystal superalloys, the weld joints are subjected to high residual stresses. These residual stresses often cause distortion and cracking of the weldments. To obtain a crack-free joint, the adverse effect of residual stresses and distortion must be kept within acceptable limits. Therefore, a thorough understanding of residual stress distribution is critical to develop successful joining processes for single crystal superalloys. In the past, a large portion of the work carried out on the residual stress distribution was accomplished by removing thin layers from the surface by chemical, electrolytic or mechanical methods. This will cause re-distribution of the stresses in the weldments. The purpose of the present investigation is to determine, by the neutron diffraction method, the internal residual stresses distribution throughout single crystal weld joint without removing surface layer. In addition, most of the research work conducted in the past has been concerned with equiaxial alloys. There is little work in the area of single crystal superalloys.

**9:50 AM**
**Spatially Resolved Residual Stress Measurements in a Welded Specimen Using Neutron Diffraction**: *Cecilia Larsson*[1]; T. M. Holden[2]; M. A.M. Bourke[2]; M. Stout[2]; L.-E. Lindgren[3]; [1]Linkoping University, Dept. of Mechl. Eng., Linkoping 581 83 Sweden; [2]Los Alamos National Laboratory, LANSCE/MST-8, Los Alamos, NM 87545 USA; [3]Lulea University of Technology and Dalarna University, Div. Compu. Aided Design, Lulea 97187 Sweden

Residual stress measurements were made on a tubular container, fabricated from a Co-based Haynes 25 alloy by welding two hemispherical end caps to either end of a cylinder. The measurements were motivated by concerns following long term exposure to heat of the container in a satellite application. Spatially resolved measurements were made using the recently commissioned Spectrometer for Materials Research at Temperature and Stress (SMARTS) at Los Alamos National Laboratory. By varying the orientation of the sample in the path of the incident neutron beam, residual strains were determined in the axial, hoop and radial directions as a function of distance from the centerline of the weld. Strains were determined by fitting single peaks in diffraction spectra as well as using entire spectra in Rietveld refinements. The maximum effective stress was determined to be around 200 MPa, well below the yield strength of the material (475 MPa). The results were compared with finite-element (FE) simulations and conclusions drawn on the effects of the welding process on the residual stress state.

**10:10 AM Break**

**10:25 AM**
**How Type-2, Intergranular, Strains Affect the Interpretation of Measured Lattice Strains in Terms of Stress Fields in Engineering Components**: *Thomas M. Holden*[1]; [1]Northern Stress Technologies, 5 Spring St., Deep River, Ontario K0J 1P0 Canada

Early neutron diffraction measurements[1] on bent steam generator tubes revealed a puzzling paradox. The apparent axial stress at the top of the bend was negative as measured with the aid of the (111) reflection of the f.c.c. structure but positive as measured with the (002) reflection at the same location. Further work with different materials and components showed such anomalies to be the rule rather than the exception. The origin of the anomalies lies in the superposition of the stresses on the length scale of the component, the type-1 stress fields, and those on the scale of the grain size, the intergranular effects. This superposition is also a contributory reason for the oscillatory anomalies seen in X-ray diffraction when strain is plotted as a function of the square of the sine of the angle of the scattering vector with respect to the surface normal. Strategies for correcting the measured lattice strains for intergranular effects are discussed for components fabricated from Inconel-600, zirconium alloys and beryllium. [1]T.M. Holden, R.A. Holt, G. Dolling, B.M. Powell and J.E Winegar, Met. Trans. A 19A (1988) 2207-14.

**10:55 AM**
**Residual Stress Measurement with Focused Acoustic Waves and Direct Comparison with X-Ray Diffraction Stress Measurements**: *Shamachary Sathish*[1]; Richard W. Martin[1]; Richard Reibel[1]; Thomas J. Moran[2]; [1]University of Dayton Research Institute, Structl. Integrity, 300 College Park, Dayton, OH 45469-0127 USA; [2]Metals, Ceramics and Nondestructive Evaluation Division, Matls. & Mfg. Direct., AFRL, WPAFB, Dayton, OH 45433 USA

The technique of measuring small changes in acoustic wave velocity due to external or internal stress have been used for quantitative determination of residual stress in materials during the last decade. Application of similar methodology with focused acoustic waves leads to residual stress measurement with spatial resolution of a few millimeters to a few microns in diameter. The high spatial resolution residual stress measurement requires development of new methodologies in both design of acoustic lenses and instrumentation for acoustic wave velocity determination. This paper presents two new methodologies developed for measurement of residual stress with spatial resolution of a few millimeters. The design of new type of acoustic lens for achieving higher spatial resolution in residual stress measurement is introduced. Development of instrumentation for high precision local surface wave velocity measurement will be presented. Residual stresses measured around a crack tip in a sample of Ti-6Al-4V; using focused beam will be compared with x-ray diffraction measurements performed on the same region of the sample. Results of residual stress measurements along a direction perpendicular to the electron beam weld in a sample of Ti-6Al-4V, determined using focused acoustic waves and x-ray diffraction technique are also presented. The spatial resolution and penetration depth of x-rays and focused acoustic beam with reference to residual stress measurements are discussed.

**11:25 AM**
**X-Ray Residual Stress Measurements in 7020 Alloy Welded Joins**: *Marzena Lech-Grega*[1]; [1]Institute of Non-Ferrous Metals, Light Metals Div., Pilsudskiego 19, Skawina 32-050 Poland

The study presents analyse of residual stresses in the around weld region of plates welded by TIG process using different welding currents in Al-Zn-Mg (7020) alloy. The residual stress by x-ray method have been measured. Dependence of welding process parameters and stress distribution was observed. The most changes in stress value in 25-40 mm zone from welded join axis have been observed and they correspond to the structure changes in this area.

**11:45 AM**
**Analysis of the Residual Stress Distribution in API X65 Steel Welded Joint Using Advanced Indentation Technique**: *Yun-Hee Lee*[1]; Dongil Son[1]; Yeol Choi[1]; Won-jae Ji[1]; Jang-Bog Ju[1]; Dongil Kwon[1]; [1]Seoul National University, Sch. of Matls. Sci. & Eng., Shinrim-Dong, Kwanak-Gu, Seoul 151-742 S. Korea

Residual stress in steel welded joint reduces the remnant lifetime of the in-field structure by degrading the fatigue and fracture properties. However, the stress evaluation is very difficult due to severe gradient of complex microstructures and mechanical properties in the welded region. Therefore, a nondestructive and local mechanical testing technique is needed. The advanced indentation technique, which has been developed for testing in local region, was used for the characterization of the welded joint. The indentation load-depth curve as the result of the test was very sensitive to the signal and the strength of the residual stress. Furthermore, the interaction between indentation stress and residual stress can be theoretically modeled. Finally, a stress-analysis equation based on the curve shift and the stress interaction parameter was proposed. The advanced indentation technique was applied to the characterization of a API X65 steel welded joint for the natural gas transmission pipeline. The evaluated stress distribution was compared with that from the saw cutting method.



## Microstructural Processes in Irradiated Materials: Multiscale Modeling I

*Sponsored by:* Structural Materials Division, ASM International: Materials Science Critical Technology Sector, SMD-Nuclear Materials Committee-(Jt. ASM-MSCTS)
*Program Organizers:* Lance L. Snead, Oak Ridge National Laboratory, Metals and Ceramics Division, Oak Ridge, TN 37830-6138 USA; Charlotte Becquart, Universite de Lille I, Laboratoier de Metallurgie Physique Et Genie des Materiaux, Villenueve síAscq, Cedex 59655 France

Tuesday AM Room: 11A
March 4, 2003 Location: San Diego Convention Center

*Session Chairs:* Robert Odette, University of California-Santa Barbara, Dept. of Mechl. Eng. & Environl. Eng., Santa Barbara, CA 93106 USA; StÈphanie Jumel, ElectricitÈ de France, MMC, Moret sur Loing 77818 France

**8:30 AM**
**Multiscale Modeling of Irradiation Embrittlment**: *G. Robert Odette*[1]; [1]University of California-Santa Barbara, Dept. of Mechl. & Environl. Eng., Santa Barbara, CA 93106 USA

Development of a comprehensive-integrated multiscale-multiphysics model of irradiation embrittlement is reviewed. Key model components include: defect production including local migration and interactions of cascade species leading to generation of cluster complexes and migrating defects - the products of long-term cascade aging; long-range diffusion of defects and solutes including trapping and in the presence of an evolving microstructure; defects and solutes annihilation and clustering; between dislocations interactions with defect complex and precipitates; hardening superposition of the irradiation-mediated and pre-existing dislocation obstacles; shifts in the toughness temperature master curve. The model provides quantitative predictions of the combined effects of irradiation (flux, fluence, temperature) and material (composition, microstructure, starting properties) variables. A detailed description of how the components of a hierarchical model are linked and the computational techniques are given. Finally, verification and calibration of the model with the enormous Irradiation Variables experiment data base are outlined.

**9:15 AM**
**Interaction of Interstitial Clusters with Impurities and a Dynamical Phase Diagram of Microstructural Evolution of Irradiated Materials**: Toby S. Hudson[1]; Maria-Jose J. Caturla[2]; Sergei L. Dudarev[3]; Adrian P. Sutton[1]; [1]Oxford University, Matls. Dept., Parks Rd., Oxford, Oxfordshire OX1 3PH UK; [2]Lawrence Livermore National Laboratory, L-353, Livermore, CA 94550 USA; [3]EURATOM/UKAEA Fusion Association, Theory & Modlg. Dept., Culham Sci. Ctr., Abingdon, Oxfordshire OX14 3DB UK

We discuss the role impurities play in the microstructural evolution of irradiated materials.† By including elastic interactions in a kinetic Monte Carlo simulation, we show trapping of one dimensionally gliding interstitial clusters both near single impurities, and in between the fields of two impurities.†Our model also allows for infrequent changes in the Burgers vector of these clusters, sometimes allowing them to escape such trapping and giving rise to three-dimensional diffusional transport. A dynamical phase diagram is constructed in order to determine under what conditions and how this trapping affects the overall microstructural evolution.†The difference between the microstructural evolution of a system with impurities with positive and negative relaxation volumes is discussed.

**9:35 AM**
**Dynamic Properties of Edge Dislocations Decorated by Interstitial Loops in a-Fe**: *Yuri N. Osetsky*[1]; David J. Bacon[1]; Bachu N. Singh[2]; [1]The University of Liverpool, Dept. of Eng., Brownlow Hill, Liverpool L69 3GH UK; [2]Risoe National Laboratory, Matls. Dept., PO Box 49, Roskilde DK-4000 Denmark

Fast thermally-activated one-dimensional glide of clusters of self-interstitial atoms (SIAs) has been observed by atomistic simulations in a variety of bcc, fcc and hcp metals. In bcc iron, for example, all SIA clusters produced in high-energy displacement cascades are glissile. This phenomenon may contribute directly to the microstructure evolution through creation of a high vacancy supersaturation due to absorption of glissile SIA clusters at sinks such as grain boundaries and dislocations, and may be responsible for the formation of specific microstructures, e.g. microvoids, void lattice, rafts of dislocation loops and decoration of dislocations by clusters and dislocation loops. The dislocation decoration is believed to play an important role in localisation of plastic deformation in irradiated materials. Possible effects have been studied recently within the framework of cascade-induced source hardening model using the isotropic elasticity theory. However, some features of the cluster-dislocation interactions cannot be described in terms of elasticity theory. It is, on the other hand, important to understand the details of these interactions since they might affect the behaviour of decorated dislocations. In this paper we present results of atomistic simulation of interactions between a moving dislocation and decoration formed by small interstitial loops with the same Burgers vector b. We have simulated an edge dislocation with b =Ω<111> gliding in {110} plane and sets of SIA clusters with size in the range 0.5-2.5nm distributed below the extra half-plane, using a many-body interatomic potential for bcc iron. The results obtained and the pinning effect of the decoration are discussed from the point of view of the cascade-induced source hardening model.

**9:55 AM Break**

**10:25 AM**
**Kinetic Monte Carlo Simulations of Precipitation Under Irradiation**: *FrÈdÈric Soisson*[1]; [1]CEA Saclay, DMN/SRMP, Gif-sur-Yvette 91191 France

The phase transformation kinetics in alloys under irradiation are now widely studied using various Monte Carlo techniques. The simulations we use are based on an atomistic description of the diffusion events. In previous studies (e.g. in the case of copper precipitation in iron) we have shown how both the details of these mechanisms and the corresponding migration barriers control the kinetic pathway of phase transformations during thermal ageing. Here we present some results concerning precipitation under irradiation, with simulations including vacancy-atom exchanges, dumbbell migration and ballistic replacement due to displacement cascades.

**10:45 AM**
**A Self-Consistent Mean-Field Theory for the Kinetics of Segregation: From Equilibrium to Irradiation-Induced Steady States**: *Maylise Nastar*[1]; [1]CEA/Saclay, DEN/DMN/SRMP, Bat. 520, Gif-sur-Yvette 91191 France

Segregation under irradiation is due to a permanent flow of vacancies and interstitials towards point defect sinks like surfaces and interfaces. A model based on a mean field lattice rate theory has already been proposed to simulate segregation in irradiated austenitic steels[1]. We complement this model with a self-consistent treatment of the mean field kinetic equations which reproduces in a natural way the up to now neglected correlation effects inherent to the vacancy diffusion mechanism[2]. Then both kinetics and thermodynamics are treated in a mutually consistent way. In particular the equilibrium properties are taken into account and we show how they contribute to the details of irradiation induced segregation profiles, e.g. the W shaped profiles. The role of the correlation effects on the kinetics and on the steady state of radiation induced segregation is discussed. [1]M. Nastar, P. Bellon, G. Martin, and J. Ruste, Phase Transformations and Systems Far from

Equilibrium, Materials Research Society Symposium Proceedings, Vol. 481, edited by E. Ma, P. Bellon, M. Atzmon and R. Trivedi (Pittsburgh, Pennsylvania Materials Research Society) p. 383, (1997). [2]M. Nastar, V. Yu Dobretsov, and G. Martin, Phil. Mag. A, Vol. 80, p.155, (2000).

**11:05 AM**
**Modeling Cascade Aging and the Formation of Vacancy-Solute Clusters in Fe-Based Alloys**: *Brian D. Wirth*[1]; Jaime Marian[1]; Eduardo M. Bringa[1]; G. Robert Odette[2]; [1]Lawrence Livermore National Laboratory, MSTD/CMS, PO Box 808, L-353, Livermore, CA 94550 USA; [2]University of California-Santa Barbara, Mechl. Eng., Santa Barbara, CA 93106 USA

Ferritic steels represent a technologically important class of materials that are widely used in current nuclear fission reactors and proposed as candidate materials for plasma-facing structures in future fusion energy facilities. Predicting their in-service performance requires a detailed understanding of the mechanisms of defect accumulation and microstructure evolution in harsh radiation environments. The physical processes involved in radiation damage are inherently multiscale, spanning more than 15 orders of magnitude in length and 24 orders of magnitude in time. In this talk, we describe multiscale modeling to predict the aging of primary defects produced in displacement cascades. The results illustrate the mechanisms responsible for the formation of i) vacancy-solute clusters which are the so-called matrix defect features in reactor pressure vessel steels, ii) <100> dislocation loops observed in ferritic steels irradiated to high dose and iii) vacancy-He clusters which serve as Helium bubble and void nuclei in fusion reactor materials.

**11:25 AM**
**Migration and Directional Change of Interstitial Clusters in a-Fe: Searching for Transition States by the Dimer Method**: *Fei Gao*[1]; Heinisch Howard[1]; Kurtz J. Richard[1]; Yuri N. Osetsky[2]; William J. Weber[1]; Richard G. Hoagland[1]; [1]Pacific Northwest National Laboratory, PO Box 999, MSIN K8-93, Richland, WA 99352 USA; [2]The University of Liverpool, Matls. Sci. & Eng., Dept. of Eng., Liverpool L69 3GH UK

Interstitial clusters produced by displacement cascades in metals exhibit thermally activated, one-dimensional glide. Only small interstitial clusters are observed to change their glide direction during the period of MD simulations. In order to overcome the ìtime barrierî in MD simulation, the dimer method is employed to search for possible transition states of interstitial clusters in a-Fe. The lowest energy barriers correspond to defect migration along <111> directions. Small clusters change their direction by a <110> dumbbell mechanism, whereas the directional change for larger clusters is a two-step process consisting of translation along a <100> direction and rotation into an equivalent <111> direction. These mechanisms are also investigated using long-time-scale MD simulations. This paper also addresses whether migrating interstitial clusters can change their directions by thermal activation under stress. The results are discussed in terms of modeling the long-time-scale dynamics of defect evolution under irradiation.

## Phase Stability, Phase Transformations & Reactive Phase Formation in Electronic Materials - III

*Sponsored by:* Electronic, Magnetic & Photonic Materials Division, Structural Materials Division, Jt. EMPMD/SMD-Alloy Phases Committee
*Program Organizers:* Sinn-Wen Chen, National Tsing-Hua University, Department of Chemical Engineering, Hsinchu 300 Taiwan; C. Robert Kao, National Central University, Department of Chemical and Materials Engineering, Chungli City 32054 Taiwan; Hyuck Mo Lee, Korea Advanced Institute of Science & Technology, Department of Materials Science & Engineering, Taejon 305-701 Korea; Suzanne E. Mohney, Pennsylvania State University, Department of Materials Science & Engineering, University Park, PA 16802 USA; Michael R. Notis, Lehigh University, Department of Materials Science and Engineering, Bethlehem, PA 18015 USA; Douglas J. Swenson, Michigan Technological University, Department of Materials Science & Engineering, Houghton, MI 49931 USA

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| Tuesday AM | Room: 12 |
| March 4, 2003 | Location: San Diego Convention Center |

*Session Chairs:* C. Robert Kao, National Central University, Dept. of Cheml. & Matls. Eng., Chungli City 32054 Taiwan; Suzanne E. Mohney, Pennsylvania State University, Dept. of Matls. Sci. & Eng., University Park, PA 16802 USA

**8:30 AM Invited**
**Electromigration Induced Phase Change in Solder Joints and Lines**: *K. N. Tu*[1]; Gu Xu[1]; Hua Gan[1]; W. J. Choi[1]; [1]University of California-Los Angeles, Dept. of Matls. Sci. & Eng., Los Angeles, CA 90095-1595 USA

Electromigration induced phase change in solder joints is unique due to eutectic alloy composition. In a eutectic alloy below the eutectic temperature, there is no chemical potential gradient as a function of composition at constant temperature and pressure. For example, there is no interdiffusion or homogenization between 70Pb30Sn and 30Pb70Sn in a diffusion couple annealed below the eutectic temperature, except ripening. Hence, electromigration can induce a very large compositional gradient in the eutectic SnPb alloy by driving Sn (near room temperature) or Pb (near 150∞C) from cathode to anode. In the up-hill diffusion, there is no reverse atomic flux to oppose electromigration due to the large concentration gradient induced by electromigration. It is different from the classic Soret effect. This eutectic effect may explain why a large amount of Cu or Ni can be dissolved from the UBM at cathode and driven to anode to from intermetallic compounds. This is because Sn-Cu and Sn-Ni also form eutectic structures of Sn and intermetallic compounds. In this talk, experimental observations of the eutectic effect will be presented.

**8:50 AM Invited**
**Electromigration Effects upon the Low-Temperature Sn/Ni Interfacial Reactions**: *Sinn-wen Chen*[1]; Chih-ming Chen[1]; [1]National Tsing-Hua University, Dept. of Cheml. Eng., Hsin-Chu 300 Taiwan

The Sn/Ni interfacial reactions at 100°C with and without the influence of passing through electric currents were studied. The intermetallic products include plate-like $NiSn_3$ and continuous $Ni_3Sn_4$ layer. The formation site of the $NiSn_3$ phase at the Sn/Ni interface is random, and its growth rate is far faster than that of the $Ni_3Sn_4$ phase. The growth of the $NiSn_3$ phase is controlled by the diffusion of the constituent Ni, and grain boundary diffusion plays an important role. Electromigration caused by an electric current of 4◊$10^3$A/cm$^2$ density has a significant effect on the $NiSn_3$ phase growth.

**9:10 AM Invited**
**Electromigration Studies of Sn96.5/Ag3.5 Flip Chip Solder Bumps**: *I. H. Chen*[1]; T. L. Shao[1]; Chih Chen[1]; [1]National Chiao Tung University, Dept. of Matls. Sci. & Eng., 1001 Ta Hsueh Rd., Hsinchu 30050 Taiwan

With environmental concerns increasing, the microelectronics industry is paying much more attention on lead-free solder alternatives. One of the most popular alternatives is Sn96.5/Ag3.5 for flip chip package. Electromigration damage of Sn96.5/Ag3.5 solder bumps was studied. Lead-free Sn96.5/Ag3.5 solder bumps were formed on a chip after printing and reflowing process. The under-bump metallization (UBM) on the chip side was Cr/Cr-Cu/Cu, and the metallurgy layer on the substrate side was Ni/Au. The chip was mounted on a BT substrate and then filled with underfill. The bumps were stressed at the current density of 2 * 10E4 A/cm$^2$ at 100°C. Whiskers and hillocks were found on the anode side, while voids were observed on the cathode side. Redistribution of atoms was examined, and composition change of intermetallic compounds was monitored. The failure mechanism of the bump after current stressing was discussed.

**9:30 AM**
**TEM Study on the Interfacial Reaction Between Electroless Plated Ni-P/Au UBM and Sn-3.5Ag Solder for Flip Chip Package**: *Eun-Jeong Kwon*[1]; Chul-Woong Yang[1]; Seung-Boo Jung[1]; Jun-Seok Ha[2]; Hee-Kwang Kang[1]; Jong-Kwon Choi[1]; [1]SungKyunKwan University, Dept. of the Adv. Matls. Eng., 300 Chonchondong, Jangan, Suwon, Kyunggi-do 440-746 S. Korea; [2]LG Electronics, Inc., 16, Woomyeong, Seoul, Seocho 137-724 Korea

Electroless Ni-P/Au deposition has attracted attention in chip package because of its simplicity of process, low cost and many good properties. But, it has not been still understood the mechanism of interfacial reaction during reflow and the information of interfacial compounds which is formed at solder joint with these two IMCs, although it seems that various Ni-Sn IMCs and Ni-P IMCs exist at the interface after soldering. Therefore, we studied on the interfacial reaction between electroless plated Ni-P/Au UBM and eutectic Sn-3.5Ag solder by using XRD, SEM, and TEM. Especially, chemical and crystallographic analysis using TEM provided us very consequential informations about microstructure of the interface. In this study, UBM is prepared by the electroless plating of Au/Ni-15at%P on Cu substrate, and then it is reacted with Sn-3.5Ag eutectic solder at 260°… for various times to examine different sequential stage of the interfacial reaction.

**9:45 AM**
**Intermetallic Compound Growth on Cu and Electroless Ni-P/Cu Substrates with Sn-5Bi-3.5Ag Solder**: *Jeong-Won Yoon*[1]; Chang-Bae Lee[2]; Seung-Boo Jung[1]; [1]SungKyunKwan University, Adv. Matls. & Process Rsrch. Ctr. for IT, 300 Chunchun-dong, Changan-gu, Suwon, Gyounggi-do 440-746 Korea; [2]Osaka University, Grad. Sch. of Eng., Suita, Osaka 565-0871 Japan

The growth kinetics of intermetallic compound layers formed between Sn-5Bi-3.5Ag solder and (Cu, electroless Ni-P/Cu) substrates were investigated at temperature between 70° and 200° for 0 to 60 days. The duplex structure of both Cu6Sn5 and Cu3Sn intermetallics existed in the couple of the Sn-5Bi-3.5Ag/Cu system, whereas the only normal Ni3Sn4 intermetallic was found on the electroless Ni-P/Cu substrate. The layer growth of intermetallic compounds satisfied the parabolic law at given temperature range. As a whole, because the values of time exponent(n) have approximately 0.5, the layer growth of the intermetallic compounds was mainly controlled by diffusion mechanism. The layer growth rate of the Ni3Sn4 intermetallic was much slower than that of the Cu-Sn intermetallic. The Ni-P deposit was a very good diffusion barrier for the Sn-5Bi-3.5Ag solder.

**10:00 AM Break**

**10:25 AM Invited**
**Solid-State Aging Reactions Between Ni and SnCu Lead-Free Solders with Different Cu Concentrations**: W. T. Chen[1]; R. Y. Tsai[1]; *C. Robert Kao*[1]; [1]National Central University, Dept. of Cheml. & Matls. Eng., Chungli City 32054 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% uncertainty in composition is generally considered acceptable. 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, during soldering, the Cu concentration had a very strong effect on the reactions between Sn-Cu solders and Ni. With increasing Cu concentration in solder, the reaction product at the interface after reflow changed from a Ni3Sn4-based compound to a Cu6Sn5-based compound. In other words, during soldering, the Cu concentration must be strictly controlled in order to obtain consistent results. In this study, we would like to extend our earlier study to investigate whether this strong concentration dependency also occurs during the solid-state aging of the solder joints. We aged solder joints at the solid-state at several different temperatures for time as long as 1000 hours. The solder compositions studied include Sn-0.2Cu, Sn-0.3Cu, Sn-0.4Cu, Sn-0.5Cu, Sn-0.6Cu, Sn-0.7Cu, and Sn-1.0Cu. Analysis techniques used include optical microscope, SEM, EPMA, and XRD. It turned out that after solid-state aging, the dependence in Cu concentration disappeared. Detailed mechanism will be presented for this interesting phenomenon.

**10:45 AM Invited**
**Intermetallic Formation Between Lead Free Solders and Ag-Pd Metallizations**: Gaurav Sharma[1]; Chad Eichfeld[1]; *Suzanne E. Mohney*[1]; [1]Pennsylvania State University, Dept. of Matls. Sci. & Eng., University Park, PA 16802 USA

We will describe the intermetallic formation between Ag-Sn and Ag-Sn-Cu solders and Ag-Pd metallizations (including pure Pd). The Ag-Pd metallization is of interest since it is used in low temperature co-fired ceramic packaging. Prolonged use of such packages at elevated temperature will likely affect the solder joints; therefore, we have studied solid state diffusion couples in these systems. Intermetallic growth was more rapid for solders on Pd compared to Ag-Pd metallizations. For the Ag-Pd metallizations, the resulting intermetallic layers were found to grow with the square root of time between 1 and 16 days, and the rate of intermetallic growth increased rapidly with temperature. For example, 59 microns of reaction product were observed after 16 days at 176∞C, whereas only 6 microns were found after 18 days at 125∞C. Rate constants and activation energies as well as the identity of the intermetallic phases will be reported.

**11:05 AM Invited**
**Stress Evolution Related with Phase Transformation During Solid State Reaction of SnAg**: J. Y. Song[1]; *Jin Yu*[1]; [1]Korea Advanced Institute of Science and Technology, Ctr. for Elect. Pkgg. Matls., 373-1 Guseong-dong Yuseong-gu, Daejon 305-701 S. Korea

In microelectronics packaging, recent trends to eliminate Pb from solders triggered intensive research on the processing method, reliability and economic issues of the Pb-free interconnection. Electroless Ni plating has been widely used as an under-bump-metallization(UBM) layer for a long time, however there has been little studies on the stress evolutions in the UBM layer during the solder reflow process. In this study, stresses in the electroless Ni UBM/electroplated SnAg solder layer due to the amorphous-to-crystalline phase transformation and the intermetallic formation were measured in-situ using laser curvature method during the solid state reaction at 200°C. The tensile stress developed and increased with time as Ni3Sn4 and Ag3Sn formed at the UBM/solder interfaces. Similarly, kinetics of phase transformation were analyzed from the stressYu evolutions during the solid state reaction, and compared with those of previous works. Finally, effects of Sn and Sn-Ag solder on the stress evolution and phase transformation of the underlying Ni layer were investigated.

**11:25 AM**
**Studies of Interfacial Reaction Between Cu Particles Reinforced SnAg Solder and Ni Thin Film UBM**: *S. J. Wang*[1]; C. Y. Liu[2]; [1]National Central University, Cheml. & Matls. Eng., No. 300, Jung-da Rd., Jung-li City, Taoyuan 320 Taiwan; [2]National Central University, Cheml. & Matls. Eng., No. 300, Jung-da Rd., Chung-Li, TaoYuang 320 Taiwan

It has been pointed out that the Cu particles reinforced SnAg composite solder has excellent mechanical properties. To use this composite solder as C4 (Controlled Collapse Chip Connections) solder bumps, we have to understand the interfacial reaction between composite solder and C4 UBM (Under Bump Metallization). Currently, we notice that Ni thin film is one of most common UBM for C4 solder joint. In this paper, we have studied the wetting reaction between Cu particles reinforced SnAg Pb-free solder and Ni thin film UBM. We will report the compound formation and kinetics of interfacial compound growth with varying thickness of Ni thin film, which are 500≈, 1000 ≈, and 2000 ≈. The preliminary results showed that Cu-Sn compound formed on the surface of Ni thin UBM, which can retard the reaction between Ni UBM and SnAg solder. No spalling was found in all Ni thin UBM with different Ni film thickness. The possible mechanism of spalling prevention will be proposed during this talk.

**11:40 AM**
**Electromigration in SnAg3.8Cu0.7 Solder Joints for Flip Chip Technology**: *Ying-Chao Hsu*[1]; T. L. Shao[1]; Chih Chen[1]; [1]National Chiao Tung University, Dept. of Matls. Sci. & Eng., 1001 Ta Hsueh Rd., Hsinchu 300 Taiwan

Lead-free SnAg3.8Cu0.7 solder will be widely used in microelectronic packaging industry due to good fatigue resistance and high joint strength. Electromigration in SnAg3.8Cu0.7 solder was investigated for flip chip solder bump structure. An under-bump metallization (UBM) of Cr-Cu/Cu/Au tri-layer was deposited on the chip side and electroless Ni/Au pad was deposited on the BT board side. Electromigration damage was observed under the current density of $2*10^4$ A/cm2 at 100°C. Voids were found at cathode side and crack was observed at solder/thin film UBM interface after current stressing. Copper and nickel atoms were found to move in the direction of electron flow. Intermetallic compounds of Cu-Sn and Ni-Cu-Sn were also observed to spread into the solder bump due to current stressing.

## Science and Technology of Magnetic and Electronic Nanostructures: Bionanoelectronics

*Sponsored by:* Electronic, Magnetic & Photonic Materials Division, Jt. EMPMD/SMD-Chemistry & Physics of Materials Committee
*Program Organizers:* Ramamoorthy Ramesh, University of Maryland, Department of Materials and Nuclear Engineering, College Park, MD 20742 USA; Y. Austin Chang, University of Wisconsin-Madison, Department of Materials Science & Engineering, Madison, WI 53706-1595 USA; Robert D. Shull, NIST, Magnetic Materials, Gaithersburg, MD 20899-8552 USA

Tuesday AM — Room: 15A
March 4, 2003 — Location: San Diego Convention Center

*Session Chairs:* Ramamoorthy Ramesh, University of Maryland, Dept. of Matls. & Nucl. Eng., College Park, MD 20742 USA; Y. Austin Chang, University of Wisconsin, Dept. of Matls. Sci. & Eng., Madison, WI 53706 USA

**8:30 AM**
**Molecular NanoElectronics**: *R. Stanley Williams*[1]; [1]Hewlett-Packard Laboratories, 1501 Page Mill Rd., MS 1123, Palo Alto, CA 94304 USA

Economic and general physics considerations indicate that the rapid improvements we have come to expect in silicon integrated circuits may saturate around the year 2010. However, fundamental physical laws indicate that it should be possible to compute with a power efficiency that is at least one billion times better than present silicon electronics. The most straightforward way currently known to achieve such efficiencies are to fabricate circuits very much smaller than they are at present. Thus, there is a tremendous business incentive to invent new electronic devices and circuits that will have dimensions of the order of nanometers. In addition, new fabrication techniques will be required that can inexpensively produce and connect these devices in vast quantities. In order to satisfy both requirements simultaneously, we have assembled a trans-disciplinary team of chemists, physicists, engineers and computer scientists at HP Labs to explore the use of molecules as active electronic devices.

**9:15 AM**

**Nanoscale Molecular Electronic Circuits**: *Yong Chen*[1]; [1]Hewlett-Packard Laboratories, 1501 Page Mill Rd., MS 1123, Palo Alto, CA 94304 USA

Within the next two decades the miniaturization of Si-based microelectronic circuits will gradually approach its scientific, technical, and economic limits. Meanwhile recent advances in molecular electronics has led to considerable promise of scaling circuits further down at nanometer scale due to the inherently small nature of molecule. In our lab, we have used molecules with bistable electronic properties to fabricate high-density memory circuits. The metal electrodes were fabricated by imprinting lithography at sub-50 nm scale. Langmuir-Blodgett molecular thin films with switchable electronic properties were sandwiched between the nanoscale metal-electrodes. Bistable electronic statues with high on-off ratio and reversible switching properties have been observed in these devices. With the nanoscale devices, fully functional high-density memory circuits were fabricated and demonstrated. The design of molecules, devices, and their circuit applications will be discussed.

**10:00 AM**

**Molecule Cascades for Computation**: *Andreas J. Heinrich*[1]; Christopher P. Lutz[1]; Jay A. Gupta[1]; Donald M. Eigler[1]; [1]IBM Almaden Research Center, 650 Harry Rd., D1, San Jose, CA 95120 USA

Molecule cascades provide new opportunities to study and utilize the controlled motion of adsorbates on surfaces. The motion of one CO molecule on a Cu (111) surface causes a nearby molecule to hop to a new site, which in turn moves another molecule, and so on in a cascade of motion similar to a row of toppling dominoes. By combining STM atom-manipulation and in-situ isotope selection we study the hopping mechanism of such molecule cascades. We find the surprising result that entire CO molecules hop by quantum tunneling at temperatures between 0.5 K and 6 K! An interesting application of molecule cascades is computation on the nanometer length scale. We show that molecule cascades can provide all of the devices and interconnects required for the one-time computation of an arbitrary logic function.

**10:45 AM**

**Biomolecular Approaches to Nanostructure Assembly**: *Anand Jagota*[1]; [1]DuPont, CR&D, E356/317A, Experimental Sta., Wilmington, DE 19880-0356 USA

This talk will describe work in our group on novel uses of biological molecules for assembly of nanostructures with application to nanoelectronic devices. Specifically, we will describe a family of peptides that bind to carbon nanotubes. These have been discovered by application of the phage display technique; binding has been verified independently. This finding offers a way by which carbon nanotubes can be functionalized by biological molecules, opening the possibilities of separation, handling, and placement. We will also describe the construction of DNA-nanoparticle assemblies where we can demonstrate remarkable control on the structure by prior control on nanoparticle size, non-specific binding, and ligand number. We will also report on nanoparticle assemblies that make use of specific protein-DNA interactions. Finally, we show how microtubules can be used as scaffolds and templates to construct conducting rods. Microtubules, which are composed of repeating units of alpha and beta tubulin, form a high aspect ratio tube about 25 nm in diameter and up to tens of microns long. We will describe techniques for metallization of the microtubule before or after immobilization on a substrate, resulting in conducting nanorods or wires.

## Surface Engineering in Materials Science - II: Surface Engineering and Modifaction

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

*Program Organizers:* Sudipta Seal, University of Central Florida, Advanced Materials Processing and Analysis Center and Mechanical, Materials and Aerospace Engineering, Oviedo, FL 32765-7962 USA; A. Agarwal, Plasma Processes, Inc., Huntsville, AL 25811-1558 USA; Narendra B. Dahotre, University of Tennessee-Knoxville, Department of Materials Science & Engineering, Knoxville, TN 37932 USA; John J. Moore, Colorado School of Mines, Department of Metallurgy and Materials Engineering, Golden, CO 80401 USA; C. Suryanarayana, University of Central Florida, Mechanical, Materials & Aerospace Engineering, Orlando, FL 32816 USA

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| Tuesday AM | Room: 7A |
| March 4, 2003 | Location: San Diego Convention Center |

*Session Chairs:* N. B. Dahotre, University of Tennessee-Knoxville, Dept. of Matls. Sci. & Eng., Knoxville, TN 37932 USA; J. Majumdar, University of Michigan, Dept. of Mechl. Eng. & Matls. Sci. & Eng., Ann Arbor, MI 48109-2125 USA

**8:30 AM Invited**

**Processing, Microstructure and Wear Properties of Ti-Base Alloys Strengthened**: *Jeff Th.M. de Hosson*[1]; [1]University of Groningen, Dept. of Appl. Physics, Matls. Sci. Ctr. & the Netherlands Inst. for Metals Rsrch., Nijenborgh 4, Groningen 9747 AG The Netherlands

In this study the Laser Melt Injection (LMI) process is explored to create a Metal Matrix Composite (MMC) consisting of 80 μm sized WC particles embedded in the top layer of a Ti-6Al-4V alloy. In particular the influences of the principal process parameters, e.g. power density, scanning speed and power flow rate, on the dimensions of the laser track and microstructural features are examined. An important finding is that the particle distribution is homogeneous and that the particles are injected over the whole depth and whole width of the melt pool. The microstructure was investigated by advanced transmission electron microscopy including energy filtering techniques and scanning electron microscopy with an integrated Electron Back-Scatter Diffraction/Orientation Imaging Microscopy (OIM). In the resolidified Ti-alloy melt pool TiC dendrites and W grains are found. Occasionally a crystal orientation relation between WC, W2C and TiC is observed, depending on the WC interface.

**9:00 AM**

**Silicon Carbide Coating on Ti-6Al-4V Alloy Using Laser Surface Modification**: *Abhijeet Prakash Joshi*[1]; Mario F. Arenas[1]; Ramana G. Reddy[1]; [1]University of Alabama, Metall. & Matls. Eng., PO Box 870202, Tuscaloosa, AL 35487-0202 USA

Ti-6Al-4V is an alloy with a wide range of applications in the aviation and space industries due to its excellent properties such as low density, high melting point, high tensile strength, good corrosion resistance and formability. However, it suffers from poor wear resistance and has a high friction coefficient, limiting its industrial widespread use. Laser surface modification provides an excellent approach for improving wear resistance. In this study, experiments were carried out using pulse Nd-YAG laser to induce melting and reaction of a powder SiC placed on the surface of the Ti-6Al-4V alloy. The experiments were performed in an inert atmosphere of argon gas. A dispersively reinforced SiC coating was formed on the surface of Ti-6Al-4V alloy. Optical microscopy, X-ray diffractometery (XRD), scanning electron microscopy (SEM), and hardness testing were used to characterize the coating formed. Results showed an improvement in wear resistance.

**9:20 AM**

**The Effects of Phosphate Treatment on Surface Friction and Coating Delamination of Galvannealed Steel**: *Doojin Paik*[1]; Gary M. Michal[1]; [1]Case Western Reserve University, Dept. of Matls. Sci. & Eng., 10900 Euclid Ave., Cleveland, OH 44106-7204 USA

Phosphate coatings on the surface of a metal during a forming operation are known to reduce surface friction. Recently phosphate has been applied to the surface of galvanneal coatings on highly formable steel sheet substrates. Such phosphate treatments have been found to both decrease surface friction and increase the amount of galvanneal coating delamination that occurs during a forming operation. To explore a possible relationship among coating delamination, surface friction and the presence of phosphate the deformation states of drawing, plane strain and biaxial stretching were applied to candidate samples.

Coating delamination was found to occur only under conditions of compressive strain. The presence of cracks in the galvanneal coatings prior to, and due to, deformation was investigated using SEM. Finally, a model was developed that takes into account the role of phosphate, preexisting cracks and how reduced surface friction can promote galvanneal coating delamination by a wedging mechanism.

**9:40 AM**

**Structures Induced by Carbon Implantation and Annealing of Tetrahedral Carbon**: *Chun Wing Lam*[1]; Igor Bello[2]; Yeshayahu Lifshitz[2]; O. Kutsay[2]; W. Y. Luk[2]; S. T. Lee[2]; X. Meng[2]; [1]City University of Hong Kong, Ctr. of Super-Diamond & Adv. Films (COSDAF) & Dept. of Physics & Matl. Sci., 83 Tat Chee Ave., Kowloon, Hong Kong China; [2]City University of Hong Kong, Hong Kong China

100 nm thick tetrahedral amorphous carbon (ta-C) films were deposited by filtered cathodic vacuum arc (FCVA). The ta-C films were then implanted with 50 keV carbon ion beam to doses ranging from 3◊10$^{13}$ to 3◊10$^{17}$ cm$^{-2}$ using metal vapor vacuum arc (MEVVA) ion source. The implanted films were annealed at various temperatures in order to form novel nanostructures being investigated upon the ion exposure with reference to the films as deposited and annealed. Considerable structural reconstruction occurred above a dose threshold of 3◊10$^{15}$ cm$^{-2}$ as indicated by Raman. Transmission electron diffraction (TED) patterns collected from the samples exposed to higher doses (above 3◊10$^{16}$ cm$^{-2}$) indicate a significant degree of preferred orientation. In correlation, electron energy loss spectroscopy (EELS) revealed the localized increase in sp$^2$ carbon bonding over the film cross-section while high resolution electron transmission spectroscopy (HRTEM) disclosed characteristic formation of graphitic basal planes preferably along the ion tracks.

**10:00 AM Break**

**10:20 AM**

**Pulsed Laser Deposited Coatings for Hydrogen and Hydrogen Isotope Permeation Resistance**: *Thad M. Adams*[1]; James Fitz-Gerald[2]; [1]Westinghouse Savannah River Company, Savannah River Tech Ctr., Bldg. 773-41A/151, Aiken, SC 29808 USA; [2]University of Virginia, Matls. Sci. & Eng., 116 Engineerís Way, Charlottesville, VA 22904 USA

The permeation of hydrogen and hydrogen isotopes is a critical issue in the operation of tritium extraction facilities and fusion reactors. To date several coating materials and materials systems have been investigate to reduce the permeation of hydrogen and hydrogen isotopes through common structural materials such as stainless steels. These materials include oxide ceramics, thermally grown oxides, metals, intermetallics, and amorphous systems. Permeation response for these coatings system has also been shown to be highly dependent on application techniques-thermal spray, CVD, EBPVD- and resulting microstructural features. The current research is focused on three coatings systems applied using pulsed laser deposition combined with laser surface modification and alloying. 304L and 316L stainless steel substrates have been coated with tungsten, aluminum oxide, chromium oxide, and Al-Fe-Ni-Nd amorphous alloy using PLD. Laser modification of the substrate has been performed in an attempt to enhance coating adhesion. Following characterization of the coating-substrate system using a field emission gun SEM, X-ray diffraction, and Auger electron spectroscopy, hydrogen-charging experiments have been carried out at 350∞C for 14 days. Additional testing has been conducted to evaluate coating behavior under thermal cycling and also under a high temperature (500∞C) humid environment.

**10:40 AM**

**Surface Modification of Graphitic Foam**: *Sharmila M. Mukhopadhyay*[1]; Erik Ripberger[2]; Ajit K. Roy[2]; Indy Roca[3]; R. Pulikollu[3]; [1]Wright State University, Mechl. & Matls. Eng., Dayton, OH 45432 USA; [2]Air Force Research Laboratory, WPAFB, OH 45433 USA; [3]Wright State University, Dayton, OH 45435 USA

Possible surface modification methods to improve the functionality of micro-cellular graphitic foams have been investigated. This solid has a complex morphology made up of graphitic planes, edges, and nanometer size structures. Since it has over 80% open interconnected porosity, the surface area per unit volume is high. This makes surface engineering the best route for targeted property modification. This paper will discuss the influence of liquid solutions and plasma coatings on foam surfaces. Surface spectroscopy studies indicate that surface oxygen fraction can be enhanced by some of these treatments, which can result in enhanced infiltration of matrix materials such as epoxy resins. Water uptake of the foam is increased by such treatments, as is the strength of foam-epoxy composites. Other treatments can result in the opposite effect, i.e. induce surface inertness, which is useful for durability of stand-alone foam structures. These results have been analyzed in light of the current state of knowledge in surface modified graphitic fibers.

**11:00 AM**

**Single-Crystal Laser Cladding of Superalloys: Influence of Preheating on the Microstructure**: *Cyrille BezenÁon*[1]; Matthias Hoebel[2]; Jean-Daniel WagniËre[1]; Wilfried Kurz[1]; [1]EPFL, CTML, CP 110, Lausanne CH-1015 Switzerland; [2]ALSTOM Power Technology, Baden CH-5401 Switzerland

The oxidation resistance of a single-crystalline Ni-base superalloy can be improved by the application of a protective layer of NiCrAlY alloy. However, current processes such as plasma spraying, produce a polycrystalline layer leading to a reduced thermo-mechanical fatigue strength of the component, due to the difference in E-modulus between clad and substrate. Therefore, a new processing allowing the deposition of a single-crystal oxidation resistant coating has been developed. In this process, the alloy powder is melted by a high intensity laser beam and solidified epitaxially onto the single crystal substrate. For a successful single-crystal deposition, nucleation and growth of misorientated grains such as stray grains must be avoided. In this paper, the influence of the substrate preheating temperature on the formation of stray crystals is experimentally determined using Electron Back-Scattering Diffraction (EBSD). It is shown that with a preheating temperature of 750∞C, nucleation of misoriented grains o ccurs in the remelted zone of the substrate and develops, into a columnar mode in the NiCrAlY layer. Processing without preheating avoids nucleation of new grains and leads to single-crystal deposition. The experimental observations are discussed with the aid of an analytical model of the columnar-to-equiaxed transition (CET).

**11:20 AM**

**Laser Surface Modification and Cell Adhesion onto Titanium Surfaces**: Steve Mwenifumbo[1]; N. Morris[2]; M. Li[3]; A. Rodriguez[2]; Seyed Allameh[1]; *W. O. Soboyejo*[1]; [1]Princeton University, Princeton Matls. Inst., D404 E. Quad., Princeton, NJ 08544 USA; [2]Princeton University, Electl. Eng., Princeton, NJ 08544 USA; [3]Spectra Physics Lasers, 1305 Tera-Bella Ave., Mountainview, CA 94043 USA

This paper presents the results of a study of cell adhesion onto Excimer laser micro-grooved surfaces. Following a brief review of the laser processing parameters required for optimum micro-groove processing, the paper explores the interactions between human osteosarcoma (HOS) cells and laser-grooved Ti-6Al-4V surfaces during the initial stages of cell spreading and adhesion. In particular, the paper examines the effects of laser groove spacing on cell/surface interactions and adhesion, which is measured with a simple cell lift-off test. The implications of the results are then discussed for the design of improved cell/surface integrity between Ti biomedical implants and the human body.

## Terence E. Mitchell Symposium on the Magic of Materials: Structures and Properties: Metallic Multilayers and Composites & Radiation Damage

*Sponsored by:* ASM International: Materials Science Critical Technology Sector, Structural Materials Division, SMD-Mechanical Behavior of Materials-(Jt. ASM-MSCTS)

*Program Organizers:* Amit Misra, Los Alamos National Laboratory, Los Alamos, NM 87545 USA; Harriet Kung, Los Alamos National Laboratory, Materials Science & Technology Division, Los Alamos, NM 87545 USA; Stuart A. Maloy, Los Alamos National Laboratory, Los Alamos, NM 87545 USA; Michael Nastasi, Los Alamos National Laboratory, Los Alamos, NM 87545 USA; Ricardo Schwarz, Los Alamos National Laboratory, Los Alamos, NM 87545 USA

Tuesday AM Room: 10
March 4, 2003 Location: San Diego Convention Center

*Session Chairs:* Harriet Kung, US Department of Energy, Div. of Matls. Scis. & Eng. USA; Mike Nastasi, Los Alamos National Laboratory, Los Alamos, NM 87545 USA

**8:30 AM Invited**

**Origins of Strength in Multilayer Composites**: *Richard G. Hoagland*[1]; Amit Misra[1]; C. H. Henager[2]; [1]Los Alamos National Laboratory, Matls. Sci. & Tech. Div., MS G755, Los Alamos, NM 87545 USA; [2]Pacific Northwest National Laboratory, Richland, WA 99352 USA

At very thin layer thickness in multilayer composites, strength ceases to obey a Hall-Petch relation, a behavior that may be, at least in metallic systems, a consequence of a transition in the nature of critical events from those involving groups of dislocations, like pile-ups, to interface crossings by single dislocations. In this paper we focus on the nonlinear atomic scale mechanisms responsible for the resistance encountered by single dislocation on crossing interfaces in fcc/fcc and fcc/bcc metallic composites. In fcc/fcc composites with small lattice mismatch, such as Cu/Ni, the limits to strength are found to be approximately equal to the coherency stress, even for semicoherent interfaces. A number of additional factors play a role, however, and include nonlinear effects on modulus, hardening due to steps, and the effect of stress on the core structures of interfacial misfit dislocations. In addition, the misfit dislocation core structures are found to be very different in Cu/Ag than Cu/Ni. In an fcc/bcc system the interface is found to contain two noncoplanar layers of misfit dislocations each with different Burgers vector. Such interfaces appear to be capable of acting both as sources and sinks for glide dislocations. This work was supported by the Office of Basic Energy Sciences, US Dept. of Energy.

**9:00 AM Invited**
**Observation of the Diffusion Processes in Annealed Cr/Cu/Ni/Au Thin-Films by Quantitative X-Ray Mapping in Analytical Electron Microscopy**: M. I. Danylenko[2]; M. Watanabe[1]; C. Li[1]; A. V. Krajnikov[2]; M. A. Vasiliev[3]; *D. B. Williams*[1]; [1]Lehigh University, Dept. of Matls. Sci. & Eng., 5 E. Packer Ave., Bethlehem, PA 18015-3085 USA; [2]Institute for Problems of Materials Science, 3 Krzhizhanivsky St., Kiev 03142 Ukraine; [3]Institute for Metal Physics, 36 Vernadsky Blvd., Kiev 03142 Ukraine

In microelectronics devices based on metallic multilayer thin-films, the thermal stability of the films in terms of the microstructure and the microchemistry is one of the most important properties. However, the thermal stability of multilayer systems is usually rather low. In a Cr/Cu/Ni/Au multilayer thin-film system, the Ni layer is usually inserted as a diffusion barrier to prevent any interactions between the Cu and Au layers since any interdiffusion between the Cu and Au layers degrades film properties. For industrial applications, control of the diffusion processes around the Ni layer are the key to improving the thermal stability in the Cr/Cu/Ni/Au multilayer system. To observe the diffusion behaviour in the annealed multilayer films, quantitative X-ray mapping has been applied using a 300keV field-emission gun analytical electron microscope. From quantified X-ray maps, the diffusion paths of Cu and Au in the Ni layer have been identified.

**9:30 AM Invited**
**The Correlation of the Deformed and Recrystallized States in Directionally Solidified Cu-Cr**: *C. W. Sinclair*[1]; J. D. Embury[2]; [1]The University of British Columbia, Dept. of Metals & Matls., Vancouver, BC V6T 1Z4 Canada; [2]McMaster University, Dept. of Matls. Sci. & Eng., Hamilton, ON L8S 4L7 Canada

A detailed study has been undertaken on the deformation of directionally solidified Cu-Cr containing 1.6at% Cr fibres that are initially dislocation free. The work hardening behaviour is dominated both by the need to load the Cr fibres until they yield at local stresses of the order of 4 GPa and the complex accommodation of large plastic strain gradients in the matrix and elastic strains in the Cr with continued plastic flow. Recrystallization of these materials provides evidence for the occurrence of ìoriented nucleationî such that similar orientations are produced at all the fibres in the array. Detailed experimental evidence and models for this process will be presented in this paper.

**10:00 AM Break**

**10:30 AM Invited**
**Effects of Simultaneous Displacive and Ionizing Radiations and Electric Field on Radiation Damage in Ionic and Covalent Crystals**: *Chiken Kinoshita*[1]; Syo Matsumura[1]; Kazuhiro Yasuda[1]; [1]Kyushu University, Appl. Quantum Physcs & Nucl. Eng., Hakozaki 6-10-1, Fukuoka 812-8581 Japan

A review is given on the formation process of radiation-induced defects and their stability under simultaneous displacive and ionizing radiations and electric field for ionic and covalent crystals. In ionic crystals such as MgO-Al2O3, retardation of dislocation loop formation, preferential formation of bubbles and retardation of amorphization are observed under simultaneous ionizing and displacive radiations. Furthermore, simultaneous irradiation with ions and electrons in the covalent semiconductors retards the accumulation of amorphous zones. The electric field, on the other hand, suppresses the formation of dislocation loops and enhances their growth in thinner specimens of ionic crystals. Those results are discussed in terms of the instability of defect clusters under electronic exciation and displacements and of the interaction between charged defects and electric fields.

**11:00 AM Invited**
**Radiation Damage Effects in Oxides**: *Kurt E. Sickafus*[1]; Robin W. Grimes[2]; [1]Los Alamos National Laboratory, Matls. Sci. & Tech. Div., MS-G755, Los Alamos, NM 87545 USA; [2]Imperial College, Dept. of Matls., Prince Consort Rd., London SW7 2BP UK

We have used atomistic computer simulations and ion beam irradiations to examine radiation damage accumulation in multi-component oxides. We have developed contour energy maps via computer simulations to predict the effects of oxide structure and chemical composition on radiation-induced atomic disorder, defect migration, and swelling. Ion irradiation damage experiments have been performed on fluorite, pyrochlore, and perovskite-structured oxide ceramics to test the predictions from computer models. This presentation will examine theoretical predictions of radiation damage behavior and the results of experimental tests using ions.

**11:30 AM Invited**
**Irradiation-Induced Solute Segregation and Precipitation: Current Status**: *Alan J. Ardell*[1]; [1]University of California, Dept. of Matls. Sci. & Eng., Los Angeles, CA 90024-1595 USA

Irradiation-induced segregation of atoms in solid solution is an important phenomenon in commercial alloys used in nuclear reactors. Grain boundaries in neutron-irradiated austenitic stainless steels eventually become depleted of Cr and enriched in Ni, with the deleterious consequence of promoting the susceptibility of the steel to stress-corrosion cracking. It is therefore not surprising that irradiation-induced solute segregation (IISS) is currently a lively topic of research in the nuclear materials community. IISS was first observed in the mid-seventies, and it was realized essentially immediately that the coupled diffusion of solute atoms and vacancies and/or interstitials to point defect sinks must play an important role in the process. Shortly after the first observations of IISS, the related phenomenon of irradiation-induced precipitation (IIP) in under-saturated alloys was discovered. This was exemplified by the unexpected heterogeneous nucleation of precipitates at dislocation loops, as well as at grain boundaries and free surfaces. Irradiation-induced homogeneous precipitation in the interior of defect-free grains of under-saturated Ni-Si alloys was also observed. As he did in so many different fields of research, Terry Mitchell made important contributions in this area as well. In this presentation the subjects of IISS and IIP will be reviewed, starting with its early history and ending with the current state-of-the art.

## The Mike Meshii Symposium on Electron Microscopy: Its Role in Materials Research: Hexagonal Materials, Intermetallics, & Ceramics

*Sponsored by:* ASM International: Materials Science Critical Technology Sector, Structural Materials Division, Japan Institute of Metals, SMD-Mechanical Behavior of Materials-(Jt. ASM-MSCTS)
*Program Organizers:* Julia R. Weertman, Northwestern University, Department of Materials Science & Engineering, Evanston, IL 60208 USA; Katherine T. Faber, Northwestern University, Department of Materials Science & Engineering, Evanston, IL 60208 USA; Morris E. Fine, Northwestern University, Department of Materials Science & Engineering, Evanston, IL 60208 USA; Wayne King, Lawrence Livermore National Laboratory, San Ramon, CA 94583-2496 USA; Peter K. Liaw, University of Tennessee, Department of Materials Science and Engineering, Knoxville, TN 37996-2200 USA; Ben Mori, Tokyo 168-0081 Japan

Tuesday AM — Room: 9
March 4, 2003 — Location: San Diego Convention Center

*Session Chairs:* T. Mori, Rutherford Appleton Laboratory, ISIS Fac., Chilton, Didcot OX11 0QX UK; P. K. Liaw, University of Tennessee, Dept. of Matls. Sci. & Eng., Knoxville, TN 37966-2200 USA

**8:30 AM Invited**
**Making Golf Easier with Titanium and Materials Science**: *E. Y. Chen*[1]; C. C. Chen[1]; F. H. Froes[2]; [1]TiTech International, Inc., 4000 W. Valley Blvd., Pomona, CA 91769-3060 USA; [2]University of Idaho, Inst. of Matls. & Adv. Processes, Moscow, ID 83844-3026 USA

The metal of the Titans is now extensively used in golf club heads allowing the weight to be strategically placed by the designer, making a user-friendly head with an oversized ìsweet spot.î As a tribute to Professor Mike Meshii for his contributions to the field of Materials Science, and to help ease him into what expects to be one of many pursuits in his well-deserved retirement, this paper discusses the application of titanium and materials science to fabricating the modern golf club head. Specific topics covered include the design and manufacture of hitting faces, often with judicious weighing using dense elements such as tungsten, processes for producing the clubs, and the evolution of materials used in golf balls. With very thin, high strength faces a major ìtrampolineî effect can be built into the head adding distance to the golferís device. Can the average golfer benefit from these advances? - Yes, although it may cost you.

**9:00 AM**
**Crystallographic and Morphological Aspects of a Laths in $\alpha$-$\beta$ Ti Alloys**: *Dhriti Bhattacharyya*[1]; Gopal B. Viswanathan[1]; Hamish L. Fraser[1]; [1]The Ohio State University, Matls. Sci. & Eng., 477 Watts Hall, 2041 College Rd., Columbus, OH 43210 USA

In alpha/beta Ti alloys, the crystallographic orientation of $\alpha$ laths and their corresponding geometrical orientations are closely linked due to the nature of the interphase boundary between the $\alpha$ (hcp) and the $\beta$ (bcc) phases and the Burgers orientation relationship (OR) between the phases. In this work, it is demonstrated that different colonies of $\alpha$ laths growing within the same $\beta$ grain could have distinctly different geometrical growth directions but could still maintain a close crystallographic relationship. It is seen that different variants of the $\alpha$ phase share a common (0001) basal plane, but are rotated only by ~10°. Similar phenomenon is also observed across two neighboring $\beta$ grains where a preference for the a colonies to have their common (0001) planes parallel to common or closely oriented {110} planes in the $\beta$ phase. TEM samples were extracted from these special boundaries using Focussed Ion Beam (FIB) for detailed analysis. Explanations for the observed phenomena are discussed based on the results obtained from Orientation Microscopy (OM), SEM and detailed TEM investigations.

**9:20 AM**
**Change in Lamellar Boundary Structure and Saturation of Yield Stress in Nano Lamellar TiAl Alloy**: *Kouichi Maruyama*[1]; Gou Suzuki[1]; Hee Y. Kim[2]; [1]Tohoku University, Dept. of Matls. Sci., Aoba-yama 02, Aoba-ku, Sendai 980-8579 Japan; [2]University of Tsukuba, Inst. of Matls. Sci., 1-1-1, Ten-nodai, Tsukuba 305-8573 Japan

Mechanical properties and lamellar boundary structure of a Ti-39mol%Al alloy with fully lamellar structure were studied at room temperature paying special attention to effects of lamellar spacing. Lamellar spacing ranging from 20nm to 600nm was made by isothermal aging at various temperatures, and most of lamellar boundaries were gamma/alpha2 boundary in the specimens. Yield stress of the alloy increases with decreasing lamellar spacing, and the Hall-Petch relation holds over the range of lamellar spacing greater than 100nm. The yield stress saturates at a value of about 1GPa below the critical lamellar spacing. TEM analysis of the lamellar boundaries revealed that misfit dislocations are introduced to the boundary when the lamella is thicker than 50nm. The saturation of yield stress will be discussed on the basis of the TEM observation of lamellar microstructures.

**9:40 AM**
**Parent-Product Interphase Boundaries and their Implications on the $\alpha$ to $\gamma_M$ Massive Transformation in Ti-Al Alloys**: Ping Wang[2]; Veer Dhandapani[3]; Mukul Kumar[4]; *Vijay K. Vasudevan*[1]; [1]University of Cincinnati, Dept. of Matls. Sci. & Eng., Cincinnati, OH 45221-0012 USA; [2]Brown University, Div. of Eng., Box D, 182 Hope St., Providence, RI 02912 USA; [3]Motorola, Inc., Digital DNA Labs., 3501 Ed Bluestein Blvd., MD K-10, Austin, TX 78251 USA; [4]Lawrence Livermore National Laboratory, 7000 East Ave., MS L-370, Livermore, CA 94550 USA

The massive-matrix interphase interfaces associated with the $\alpha$ to $\gamma_M$ massive transformation in Ti-(46-48)Al alloys were studied. Special experiments were performed to arrest the transformation at an early stage. Nucleation and growth kinetics were determined and the former compared with calculations for various nuclei shapes using classical nucleation theory. Orientation relations between the $\gamma_M$ and parent $\alpha$ (retained $\alpha_2$) phases were determined using EBSD in an SEM and by electron diffraction, and the interphase interfaces and defect structures in the $\gamma_M$ phase characterized by two-beam bright-field/weak-beam dark-field TEM and HRTEM. The results reveal that the $\gamma_M$ nucleates at grain boundaries with a low-index orientation relation and coherent interface with one parent grain, but grows into the adjacent grain with a high-index/irrational orientation relation. The growth interfaces between the two phases are generally free of misfit dislocations and consist of curved parts as well as planar facets whose macroscopic habit varies from high-index/irrational to low-index orientation. On an atomic scale the growth interfaces are occasionally found to be faceted along {111} planes with steps, but are incoherent with respect to the parent grain into which growth occurs. The implications of these results on the nucleation and growth mechanisms associated with the $\alpha$ to $\gamma_M$ massive transformation will be discussed. The authors are grateful for support of this research by the National Science Foundation under grants DMR-9224473 and 9731349, Dr. Bruce MacDonald, Program Monitor.

**10:00 AM**
**Scanning Electron Microscopy of Natural Ice**: *I. Baker*[1]; D. Cullen[1]; D. Iliescu[1]; R. Obbard[1]; [1]Dartmouth College, Thayer Sch. of Eng., 8000 Cummings Hall, Hanover, NH 03755 USA

The microstructural location of impurities in natural polycrystalline ice has been of interest for over a century. Recently, we have developed a technique to determine the microstructural location of impurities in ice that involves controlled preferential sublimation of ice in a low-vacuum scanning electron microscope equipped with a nitrogen gas-cooled cold stage. The sublimation leaves behind concentrated impurities, which can be identified using x-ray microanalysis. In this presentation, observations on specimens from Greenland, Antarctica, and pond and river ice will be presented. The polar ice cores showed impurities such as Cl, S and less-commonly Na, Ca and Mg throughout the material. In the ice from Greenland, filaments consisting chiefly of NaCl were observed in the grain boundaries (GBs). These are thought to form by coalescence of the impurities that were located in the GB plane. The grain interiors of the lake and river ice also contained impurities. However, in river ice, most of the impurities were located in inclusions of ≤ 20 µm diameter in the GBs. In contrast, the pond ice contained many unusually-shaped, but often facted, hexagonal-symmetry features from 200-1000 µm in diameter that were usually located in or near the GBs. These features appear to simply be small ice crystals that have nucleated on impurities. This research was supported by US National Science Foundation grant OPP-9980379 and Army Research Office grant DAAD 19-00-1-0444.

**10:20 AM**
**Grain Size Hardening and Softening in Intermetallic Compounds at Low Homologous Temperatures**: *Hans Conrad*[1]; Jay Narayan[1]; [1]North Carolina State University, Matls. Sci. & Eng., Raleigh, NC 27695-7907 USA

Results by the authors on the effect of grain size on the hardness of laser-deposition WC and TiN films with grain sized in the range of 6-46 nm are presented and compared with data in the literature for these materials and other intermetallic compounds. Three grain size regimes were identified: Regime I (d=10^-6-10^-3m), Regime II (d=10^-8-10^-6m) and Regime III (d<10^-8m). Regimes I and II are characterized by grain size hardening (Hall-Petch effect) governed by intragranular dislocation activity, Regime III by grain size softening (inverse Hall-Petch effect) characterized by the absence of intragranular dislocation activity and resulting from grain boundary shear. The mechanisms governing each of the regimes are discussed.

**10:40 AM Cancelled**
**Comparison Between Microstructures of Conventional and New Raney Catalysts**: *Jose G. Cabanas-Moreno*[1]; Beatriz H. Zeifert[1]; Hector A. Calderon[1]; J. B. Salmones[2]; [1]ESFM-IPN, Ciencia de Materiales, Apdo. Postal 75-707, Mexico DF 07300 Mexico; [2]Instituto Mexicano del Petroleo, Eje Central Lazaro Cardenas 152, Mexico, DF 07730 Mexico

**11:00 AM**
**Influence of Si Content and Sputtering Condition on the Microstructure and Mechanical Properties of r.f.-Sputtered Transition Metal Nitride Films**: *Masateru Nose*[1]; Wen-An Chiou[2]; Yutaka Deguchi[3]; Takehiko Mae[4]; Kiyoshi Nogi[5]; Mike Meshii[6]; [1]Takaoka National College, Dept. of Industl. Arts & Crafts, 180 Futagami-machi, Takaoka, Toyama 933-8588 Japan; [2]University of California-Irvine, Dept. of Cheml. Eng. & Matls. Sci., 636E Engineering Tower, Irvine, CA 92697-2575 USA; [3]Toyama University, Grad. Sch. of Sci. & Eng., 5190 Gofuku, Toyama 930-8555 Japan; [4]Toyama National College of Technology, Dept. of Environl. Matls., 13 Hongo-machi, Toyama 939-8630 Japan; [5]Osaka University, Joining & Welding Rsrch. Inst., 11-1 Mihogaoka, Ibaraki, Osaka 567-0047 Japan; [6]Northwestern University, Dept. of Matls. Sci. & Eng., 2225 N. Campus Dr., Evanston, IL 60208-3108 USA

The influence of Si content and sputtering condition on the microstructure and mechanical properties (hardness and Youngís modulus) of transition metal nitride films such as ZrSiN and TiSiN were investigated using XRD, TEM and nanoindentor. While the substrate was heated from room temperature to 673 K during deposition, some films were applied with d.c.-bias voltage. Without substrate heating and bias application, the hardness of the films increased for 5-10 GPa over binary system such as ZrN or TiN with a small amount (3-5 at%) of Si;

it then decreased to a hardness lower than those of binary systems when Si was more than 10 at%. The tendency to grow columnar grains was strongest at a ~ 3-5 at% of Si, but it became equiaxial when Si was > 5 at%. However, nano-crystal and/or amorphous like structure were formed if Si was > 10 at%. The increase of hardness with small additional amount of Si to metal nitride films is probably attributed to the atomic strain caused by Si atoms at nonequilibrium sites. These results also indicate that the grain size can be of minor contributions to the hardening. The influences of the sputtering conditions will also be discussed.

**11:20 AM**
**HREM Analysis of γí Particles in Late Stages of Coarsening in Ni Alloys**: Lorenzo Calzado-Lopez[1]; T. Mori[2]; Christian Kisielowski[3]; *Hector A. Calderon*[1]; [1]ESFM-IPN, Ciencia de Materiales, Apdo Postal 75-707, UPALM Ed 9, Mexico, DF 07300 Mexico; [2]Rutherford Appleton Laboratory, ISIS Fac., Chilton, Didcot OX11 0QX UK; [3]Lawrence Berkeley National Laboratory-National Center for Electron Microscopy, Berkeley, CA 94720 USA

Coarsening of coherent particles in solid matrices apparently leads to particle splitting after a given critical size. Experimentally symmetrical particle arrangements have been used to demonstrate the occurrence of splitting but little has been done regarding kinetics or the development of particle size distributions (PSD) after splitting. This investigation deals with determination of order domains in γí particles by high resolution electron microscopy (HREM). Several Ni base alloys have been used (model and commercial) in the late stages of coarsening where a critical size for splitting is expected. Nevertheless the present results show that most particles (around 85%) in a variety of arrangements and sizes, have different order domains. This suggests that splitting has not taken place since otherwise particles in a given group would have an identical order domain. On the other hand, both kinetics and PSD show an smooth development without any indication of splitting.

**11:40 AM**
**Dislocation Activity During Superplastic Flow in the Zn-22% Al Alloy**: *Yuwei Xun*[1]; Wen-An Chiou[1]; Farghalli A. Mohamed[1]; [1]University of California-Irvine, Dept. of Cheml. Eng. & Matls. Sci., Irvine, CA 92697-2575 USA

An investigation was conduced on the superplastic Zn-22% Al alloy that contained nanometer-scale dispersion particles, which were introduced into the microstructure by powder metallurgy. In the investigation, specimens were crept at a strain rate near the center of the superplastic region, which represents region II (the intermediate-stress region), in the sigmoidal plot between stress and strain rate that was reported for the alloy. Preliminary transmission electron microscopy (TEM) observations reveal evidence of lattice dislocation activity. This evidence is demonstrated by the presence of particle-dislocation interactions in the interiors of the grains of the alloy. The results are discussed with reference to various deformation mechanisms proposed for micrograin superplasticity.

## Yazawa International Symposium on Metallurgical and Materials Processing: Principles and Technologies: Metals and Sulfide Systems

*Sponsored by:* Extraction & Processing Division, EPD-Process Fundamentals Committee, EPD-Pyrometallurgy Committee, EPD-Aqueous Processing Committee, EPD-Copper, Nickel, Cobalt Committee, EPD-Lead and Zinc Committee, Jt. MPMD/EPD-Process Modeling Analysis & Control Committee; See Plenary Session for Co-Sponsors

*Program Organizers:* Hong Yong Sohn, University of Utah, Department of Metallurgical Engineering, Salt Lake City, UT 84112-0114 USA; Kimio Itagaki, Tohoku University, Institute for Advanced Materials, Sendai 980-8577 Japan; Florian Kongoli, FLOGEN Technologies, Inc., Materials Technology Department, Montreal, Quebec H3S 2CS Canada; Chikabumi Yamauchi, Nagoya University, Department of Materials Science & Engineering, Nagoya 464 8603 Japan

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| Tuesday AM | Room: Solana |
| March 4, 2003 | Location: San Diego Marriott Hotel |

*Session Chairs:* R. Hurman Eric, University of the Witwatersrand, Sch. of Process & Matls. Eng., Wits 2050 S. Africa; Seshadri Seetharaman, Royal Institute of Technology, Div. of Metall., Stockholm SE-100 44 Sweden

**8:30 AM Keynote**
**Solute Interactions with Dissolved Oxygen in Molten Copper Systems**: *Seshadri Seetharaman*[1]; Patrik Fredriksson[1]; Ragnhild Aune[1]; [1]Royal Institute of Technology, Div. of Metall., Stockholm SE-100 44 Sweden

In fire refining of copper, the affinities of various impurity elements on dissolved oxygen is of great significance. Further, in the design of oxygen probes in liquid copper, the influence of solute interactions on the activity of oxygen need to be considered in order to evaluate the oxygen concentration in molten copper. The present paper presents a series of measurements of the activities of oxygen in liquid Cu-M-O alloys (where M stands for Mn, Zn, As, Se or Te) carried out by the present group employing the solid electrolyte galvanic cell technique. Extreme care was taken to control the oxygen potentials in the inert gas atmosphere, and to keep the oxygen levels very low in the molten metal. The oxygen content was determined by analysis of the samples taken out from the melt. The results obtained showed that Mn has a strong negative influence on the activity coefficient of oxygen in liquid copper. A similar, but less prominent effect was observed in the case of Zn. Arsenic had no influence on the activity of oxygen in Cu (liq.). Se and Te had slight negative effect on oxygen activities in copper at $X_O 10^{-5}$, while at lower oxygen levels the interaction coefficients were found to be positive. The results obtained were compared with empirical models for the calculation of interaction coefficients available in literature.

**9:05 AM**
**Desulfurization Kinetics of Molten Copper Matte by Gas Bubbling**: H. Sang Sohn[2]; Yasuhiro Fukunaka[1]; Toshio Oishi[3]; [1]Kyoto University, Dept. of Energy Sci. & Tech., Sakyo-ku, Kyoto 606-8501 Japan; [2]Kyungpook National University, Dept. of Matls., Daegu 702-701 Korea; [3]Kansai University, Dept. of Matls. Eng., Suita 564-8180 Japan

The kinetic study on desulfurization of copper matte by gas bubbling was designed under the presumptions of lower FeO activity and of no fayalite slag formation. Copper matte with 59% Cu and 22.6% S in weight ratio was oxidized at 1523K by bubbling of Ar+O2 gas through a submerged nozzle. The effects of oxygen partial pressure and flow rate of gas on the oxidation rate of matte were discussed. The desulfurization rate and evolution rate of SO2 gas of copper matte were influenced by the oxygen partial pressure. However, they were confounded each other. The desulfurization rate and evolution rate of SO2 gas of copper matte were described by the mass transfer rate through the gas film around the rising gas bubbles. The calculated results reasonably describe the observed desulfurization rate and evolution rates of SO2 gas at a constant oxygen partial pressure of 0.2 atm.

**9:30 AM**
**Phase Equilibria and Thermodynamics in the Ag-Pb-S Ternary System**: *R. Hurman Eric*[1]; Hakan Ozok[1]; [1]University of the Witwatersrand, Sch. of Proc. & Matls. Eng., PB 3, Wits, Johannesburg, Gauteng 2050 S. Africa

Within the Ag-Pb-S ternary system, the boundaries of the immiscibility region together with the tie-line distributions were re-established at 1198K by the equilibration-quenching technique where samples were kept in evacuated and sealed silica capsules. Activities of Pb were measured by the dew-point method along the Ag-Pb binary at 1198, 1373 and 1473K. Positive deviations were observed and the results were modelled by the Krupkowski formalism. Activities of Ag, Pb, and S, along the ternary miscibility gap were calculated at 1198K by utilizing the bounding binary thermodynamics, phase equilibria and tie-lines. Activities of Pb were also measured along the metal-rich boundary of the miscibility gap to confirm the calculated Pb activities at 1198K.

**9:55 AM**
**Activities of the $Cu_2S$-FeS System Calculated from the Data of the $Cu_2S$-FeS-$Sb_2S_3$ System**: *Grigore Matei*[1]; Yasushi Takasaki[2]; Kimio Itagaki[3]; Kazuo Koike[2]; [1]University ìPolitehnicaî of Bucharest, Matls. Sci. & Eng. Fac., Spl. Independentei 313, Bucharest Romania; [2]Akita University, 1-1 Gakuen-Cho, Tegata, Akita 010-8502 Japan; [3]Tohoku University, 2-1-1 Katahira, Aoba-Ku, Sendai 980-8577 Japan

The thermodynamic property of the $Cu_2S$-FeS system is important not only in the case of copper smelting but also in the case of general pyro-metallurgy. However, there are not many reported activity data. In this study, activities of $Cu_2S$ and FeS in the $Cu_2S$-FeS system were calculated using the Darkenís method from the activity data of the $Cu_2S$- FeS-$Sb_2S_3$ system measured by the transportation method at 1050°C. The activities of $Cu_2S$ and FeS in the $Cu_2S$-FeS system showed negative deviation from the ideal behavior and satisfied the relation of the Gibbs-Duhem equation.

**10:20 AM Break**

**10:40 AM Invited**

**High Temperature Thermodynamic Studies on Sulfide Systems Using the Dew Point Technique**: *R. Hurman Eric*[1]; [1]University of the Witwatersrand, Sch. of Process & Matls. Eng., PB 3, Wits 2050 S. Africa

The dew-point technique of activity measurements take advantage of the volatility of a component in solution. The pressure of the volatile component over a sample is determined from observations of the temperature at which condensation of the vapor occurs. The method is applicable best when the vapor pressure of the components would differ by about two to three orders of magnitude. Experimentally, this is a closed system involving the use of evacuated and sealed transparent quartz sample probes. Furthermore reliable vapor pressure data of the volatile component is essential along with a specialized high temperature furnace capable of giving reproducible results. In this context, the vertical Dew-Point Furnace (DPF) was designed and built after elaborate trials until enough proficiency was gained for reproducible results. Over the years the DPF was modified and improved. The DPF developed was versatile and could easily be used for activity measurements in the isopiestic mode (another method of measuring activities of a volatile component in a solution). The necessary ancillary systems; namely evacuation-flushing-evacuation followed by sealing of quartz sample probes under vacuum were also perfected over the years. As and when necessary the dew-point technique was supplemented by classical equilibration-quenching method employed on sealed quartz sample probes to reveal necessary phase equilibrium information. The following were studied utilizing the above technique: (i)Activities in $Cu_2S$-PbS and FeS-PbS binary and $Cu_2S$-FeS-PbS ternary at 1200°C, (ii)Phase equilibria and thermodynamics in the Pb-PbS system, (iii)Phase equilibria and thermodynamics in the Cu-Pb-S and Fe-Sn-S systems, (iv)Activities in FeS-SnS and $Ag_2S$-SnS binary and FeS-$Cu_2S$-SnS ternary at 1200°C,(v)Phase equilibria and thermodynamics in Ag-Pb, Fe-Pb-S, Ag-Sn-S and Ag-Pb-S systems. Most recently the following systems have been tackled: Phase equilibria and thermodynamics in the Sn-Pb-S system and activities in $Ag_2S$-PbS binary, $Ag_2S$-$Cu_2S$-PbS and $Ag_2S$-FeS-PbS ternaries and $Ag_2S$-$Cu_2S$-FeS-PbS quaternary at 1200°C.

**11:10 AM**

**Thermodynamic Properties of Copper-Nickel Mattes**: *L. Sh. Tsemekhman*[1]; A. V. Tarasov[2]; V. M. Paretsky[2]; [1]AO ìGipronickelî, 1 Grazhdansky Pr., Saint-Petersburg 195220 Russia; [2]"GINTSVETMETî, 13 Acad. Korolyov St., Moscow 129515 Russia

Studies into thermodynamic properties of Cu-Ni and Cu-Ni-S systems and mattes have been conducted with the aid of a MC-1301 mass-spectrometer designed for investigation of processes of vapor formation of difficult-to-volatilize substances. The instrument constitutes a combination of an evaporator of Knudsen chamber type and a mass-spectrometric analyzer of vapor phase. Effusion Knudsen chambers were preliminarily calibrated based on the silver and gold vapor pressure recommended as IUPAC pressure standards. Partial pressures of vapor components were determined, depending on the objective set, by the method of complete isothermal evaporation or the ion current comparison method. Measurements of temperature relationship of the ion current intensity of Cu+ and Ni+, as well as atomic copper vapor pressure above molten copper and atomic nickel vapor pressure above solid nickel metal using the method of complete isothermal evaporation made it possible to define equations of the effect of temperature within a range of 1400K to 1800K on copper and nickel vapor pressures. The process of copper-nickel system evaporation within the entire range of compositions had a clear-cut incongruent character and the intensity of ion current of Cu+ during the test period decreased, while that of Ni+ increased. When studying the Cu-Ni-S system, the sulfur partial pressure was measured by the complete isothermal evaporation method and the copper and nickel partial pressure was measured by the ion current comparison method. The values of partial pressures of components above the Cu-Ni-S melt were used for calculation of activities of these components in the melt. The copper and nickel activity data were used for assessment of the value of soluble losses of these metals in slag of autogenous smelting. Studies of evaporation processes of commercial-grade mattes were carried out at a temperature of 1500K. As a result of processing of experimental data, relationships of partial pressures of copper, iron and sulfur were obtained, which are valid for the following ranges of compositions, % at.: 0.3-15.4 Cu, 35.2-80.6 Fe and 10.4-30.7 Ni. <p>PCu = 1.35 - 0.034[Cu] - 0.013[Fe] - 0.014[Ni] (1) P = 1.52 - 0.039[Cu] - 0.015[Fe] - 0.010[Ni] (2) PFe◊10-2 = 1.10 - 0.024[Cu] + 0.004[Fe] - 0.039[Ni] (3) <p> Activity values and activity coefficients of nickel have been calculated on the basis of the data obtained.

**11:35 AM**

**Determination of the Degree of Oxidation of Molten Copper Using an Electrochemical Cell**: *JosÈ Alberto V·zquez-Monroy*[1]; JosÈ Antonio Romero-Serrano[1]; Mario Alberto GarcÌa-GarcÌa[1]; Samuel Ganz·lez LÛpez[1]; [1]E.S.I.Q.I.E-IPN, Metallurgl. Eng., Unidad Profesional Adolfo Lopez Mateos, Lab. Pesados de Metalurgia, MÈxico D.F. 07738 MÈxico

Copper is the third most widely used metal in terms of tonnage per year throughout the world, after iron and aluminum. Copper is an excellent conductor of electricity and heat, only slightly exceeded by silver. The electrical conductivity of copper explains its the sharp increase with the arrival of the age of electricity. At the present, almost 75% of copper consumption goes into this type of usage. The high temperature galvanic cells have come into prominence on account of their numerous applications in both fundamental and applied measurements. Since the inception of the oxygen-ion conducting electrolytes like ZrO2-CaO, the oxygen concentration cells have been extensively used in laboratories as well as in industries. In metal production technology, these cells have been used to monitor the oxygen potentials in metals. The pioneer among the various industrial users of such cells is the copper industry. Today, high temperature solid electrolyte cells involving oxygen ion conducting electrolytes have become an integral part of copper pyro-refining and continuous casting, because it is possible to control the oxygen level and to predict the amount of other alloy elements. For these reasons, in the present paper the degree of molten copper oxidation was determined in terms of the amount of Cu3P used as deoxidant, the particle size of Cu3P and temperature. The oxygen sensor was prepared with Zirconia Stabilized with Itria (ZEI), using Ni-NiO as reference electrode. The first part of this study consisted of developing an electrochemical cell to measure the oxygen activity in molten copper. The second part consisted of a thermodynamic analysis, which was carried out with a commercial software FACT (Facility for the Analysis of Chemical Thermodynamics). This software has databases of pure substances and systems in solution and can be used to study complex process like the Copper production. The thermodynamic study allowed to relate the oxygen activity and its concentration. Finally it was developed a model of dissolution of Cu3P in the bath in terms of the reaction time and temperature, which allows to estimate the dissolution rate of Cu3P particles in the melt.

## Yazawa International Symposium on Metallurgical and Materials Processing: Principles and Technologies: Aqueous and Electrochemical Processing II

*Sponsored by:* Extraction & Processing Division, EPD-Process Fundamentals Committee, EPD-Pyrometallurgy Committee, EPD-Aqueous Processing Committee, EPD-Copper, Nickel, Cobalt Committee, EPD-Lead and Zinc Committee, Jt. MPMD/EPD-Process Modeling Analysis & Control Committee; See Plenary Session for Co-Sponsors

*Program Organizers:* Hong Yong Sohn, University of Utah, Department of Metallurgical Engineering, Salt Lake City, UT 84112-0114 USA; Kimio Itagaki, Tohoku University, Institute for Advanced Materials, Sendai 980-8577 Japan; Florian Kongoli, FLOGEN Technologies, Inc., Materials Technology Department, Montreal, Quebec H3S 2CS Canada; Chikabumi Yamauchi, Nagoya University, Department of Materials Science & Engineering, Nagoya 464 8603 Japan

Tuesday AM Room: Pacific
March 4, 2003 Location: San Diego Marriott Hotel

*Session Chairs:* Yoshiaki Umetsu, Tohoku University, Inst. of Multi. Rsrch. for Adv. Matls., Sendai 980-8577 Japan; Rafael Padilla, University of ConcepciÛn, Metallurgl. Eng., ConcepciÛn Chile

**8:30 AM Keynote**

**Environmentally Friendly Route to Copper Production: Sulfidation and Leaching of Chalcopyrite Concentrates**: *Rafael Padilla*[1]; [1]University of ConcepciÛn, Metallurgl. Eng., Edmundo Larenas 270, ConcepciÛn Chile

In the production of copper from chalcopyrite (CuFeS2) concentrates by the smelting and converting technology, the ambient pollution with gaseous SO2 and toxic metals such as arsenic compounds is still a serious problem, especially in the converting step due to the batch nature of the conventional Peirce Smith process. Non-SO2 emitting alternatives are leaching processes. However, few of them have had a limited industrial application and they are not very effective in discarding safely the toxic impurities. A combination of pyro-hydrometallurgical methods: the sulfidation of chalcopyrite and subsequent leaching of the sulfidized material is a non-polluting alternative to treat not only clean chalcopyrite concentrates but also complex chalcopyrite-enargite concentrates. In this article, this alternative is discussed concerning the thermodynamics and kinetics of the sulfidation of chalcopyrite with gaseous sulfur. The kinetics of the leaching of the sulfidized concentrate in an H2SO4-NaCl-O2 system is also discussed.

**9:05 AM**

**Construction of Electrical Conductivity of Copper Sulfate Electrolytes Acidified with Sulfuric Acid for Copper Electrorefining and Electrowinning Processes**: *Kazuteru Tozawa*[1]; Yoshiaki Umetsu[2]; Quing-Quan Su[3]; Zi-Qiang Li[4]; [1]Tohoku University, Sendai 980-0845 Japan; [2]Tohoku University, Inst. of Multi. Rsrch. for Adv. Matls., Sendai 980-8577 Japan; [3]Ebara Corporation, Tokyo 144-8510 Japan; [4]Chandu Science and Technical University, Chandu China

The electrical conductivity of electrolytes for copper electrorefining and electrowinning processes has been reported by many researchers since 1911. The experimental results show that the conductivity increases with an increase in sulfuric acid concentration, but decreases with an increase in copper concentration. In pure copper sulfate solution, however, the conductivity increases with an increase in copper concentration. After confirming the conductivity of pure and acidified copper sulfate solutions experimentally, we found that the conductivity of acidified copper sulfate electrolytes is mainly controlled by concentrations of hydrogen ion and free (not hydrated) water. It can be explained on the basis of the finding that the conductivity of copper sulfate electrolytes acidified with sulfuric acid decreases with an increase in copper concentration.

**9:30 AM**

**Separation of Copper and Arsenic from Copper-Arsenic-Sulfuric Acid Electrolytes by Using Electrodialysis**: *J. P. Ibanez*[1]; C. Gutierrez[1]; L. Cifuentes[2]; [1]Arturo Prat University, Dept. of Metall., Av. Arturo Prat 2120, Iquique Chile; [2]Universidad de Chile, Dept. of Mining Eng., Av. Tupper 2069, Santiago Chile

The separation of arsenic and copper from Cu-As-H2SO4 electrolytes by using electrodialysis was investigated at ambient temperature in a laboratory batch cell. The effect of current density and pH were studied. A solution of copper free of arsenic was obtained by this technique at all the conditions investigated. The efficiency for the transport of Cu2+ was found to reach values higher than 98% in 3 hours. The transport of arsenic and copper through the ion exchange membranes was favored by increasing the pH and by increasing the current density. The pH of the system was found to be a key parameter for the process, since it controls the speciation of the ions to be transported and the formation of unwanted precipitates that reduced the global efficiency of the electrodialysis process. The main conclusion of the work is that the electrodialysis is a promising technique to be used in separating and/or concentrating ions of interest in electrometallurgical plants of copper.

**9:55 AM**

**Effect of Fe(II), Co(II) on the Formation of Lead and Manganese Oxides During Copper Electrowinning**: *A. Pagliero*[1]; F. Vergara[1]; J. Ipinza[2]; J. L. Delplancke[3]; [1]University of ConcepciÛn, Dept. of Metallurgl. Eng., Edmundo Larenas 270, PO Box 53-C, ConcepciÛn 00187 Chile; [2]University Arturo Prat, Dept. of Metallurgl. Eng., Arturo Prat 2120, PO Box 121, Iquique Chile; [3]University Free of Brussels, Fac. of Appl. Scis., 50 Av. F.D. Roosevelt, CP 194/03, Brussels B-1050 Belgium

Small manganese concentration and other impurities ($Fe^{2+}$,$Al^{3+}$) in the high acid electrolyte are transferred to copper electrowinning. Experimental test of electrolysis were conducted a 50∫C in 180 g/L $H_2SO_4$ to investigate the behavior of manganese and iron in solution on the film stability of the alloy PbCaSn. The effects of ions such as $Fe^{2+}$, $Co^{2+}$ in acidic electrolytes with manganous ions on the anode corrosion were investigated. These impurities were found to affect the anode PbCaSn corrosion. The presence of 4g/L $Fe^{2+}$ in the electrolyte and different manganese concentration in the rank 0.07 to 4 g/L, inhibit the formation of slimes formed by $\beta$-$MnO_2$ tetragonal (disproportionation reaction). However, the layer of $MnO_2$ amorphous formation on the lead oxides is uninterrupted but its thickness is very thin. This condition aid the dissolution of the $PbO_2$. The corrosion of PbCaSn anode is much less when it is compared to media containing only cobalt and manganese.

**10:20 AM Break**

**10:35 AM Invited**

**Surface Tension, Density and Viscosity Coefficient of Acidic Copper Sulfate Solution Simulating Electrolyte Solution for Electrolytic Copper Production With/Without Addition of Gelatin**: Kazuteru Tozawa[1]; Quing-quan Su[2]; *Yoshiaki Umetsu*[3]; [1]Tohoku University, Sendai 980-0845 Japan; [2]Ebara Corporation, Tokyo 144-8510 Japan; [3]Tohoku University, Inst. of Multidisciplinary Rsrch. for Adv. Matls., 1-1 Katahira 2-chome, Aoba-ku, Sendai 980-8577 Japan

Surface tension, density and viscosity coefficient of the acidic copper sulfate solutions simulating electrolyte solution for copper electrorefining has been measured and are summarized as a function of the solution composition and temperature. Nickel sulfate is taken to be a representative coexisting sulfate affecting the physical properties of the electrolyte solution. The sulfates in the solutions including sulfuric acid increase the values of physical properties under consideration. Gelatin, representing organic additives for electrolyte solution, was found to sensitively affect the surface tension of the solution at low concentration less than 200mg/L. The surface tension was markedly lowered by addition of gelatin and the higher concentration of gelatin led to more pronounced decrease in the measured values. The surface tension gradually increased with time after addition of gelatin and the increment was enhanced by higher acid concentration and higher temperature. The observed change in the surface tension is considered to reflect preferential adsorption of gelatin to the solution surface and decomposition of gelatin due to hydrolysis to form various molecules having smaller molecular weights.

**11:05 AM Invited**

**The Mechanism of Sphalerite Dissolution in Ferric Sulphate-Sulphuric Acid Media**: *A. Pratt*[1]; J. E. Dutrizac[1]; T. T. Chen[1]; [1]CANMET, 555 Booth St., Ottawa, Ontario K1A OG1 Canada

Fracture exposed surfaces of sphalerite samples having five different iron contents ranging from approximately 0 wt% to 14.8 wt% Fe were leached from 15 to 120 seconds at idd0c in 0.3 M $Fe(SO4)_{1.5}$-0.3 M $H_2SO_4$ media. The reacted samples were examined using X-ray photoelectron spectroscopy (XPS) which provides chemical state information on the first few nanometers of the solid surface. Surface compositions obtained from reference and leached sphalerites show that the leaching rate increases with increasing iron content. Detailed evaluation of high resolution S2p spectra show that the leaching progresses via the formation of polysulphide species. Disulphide species were not detected in any of the experiments. Examination of the Zn2p and Fe2p spectra show little change in the chemical states over the duration of these experiments. Longer leaching times resulted in the generation of elemental sulphur. The ratios of elemental sulphur to dissolved ferrous ions and zinc suggest that less than 5% of the sulphide is oxidized to sulphate, for zinc extractions ranging from 8 to 100%. Morphological studies showed that the elemental sulphur initially formed at a few isolated sites, such as the grain boundaries Furthermore, faceted euhedral sulphur crystals were often identified. These observations suggest that at least part of the elemental sulphur forms via dissolved sulphide species which are oxidized in solution by the ferric sulphate.

**11:35 AM**

**Technological Flowsheet of Sulfide Copper Concentrates Treatment as Non-Ferrous Metals Production By-Products**: *Y. M. Shneerson*[1]; A. Y. Lapin[1]; T. Y. Kositskaya[1]; K. A. Muravin[1]; L. V. Chugaev[1]; [1]Norilsk Nickel RJS, Gipronickel Institute JS, Saint-Petersburg Russia

At Gipronickel Institute the technological flowsheet of pressure leaching of copper from rich copper concentrates (i.e. containing: Cu -59-75%; Ni -0.5-4.64%; Fe -0.2-1.3%; S -21.8-26.9%) was developed. As a result, the possibility of deep decomposition of copper-containing minerals with extraction of elemental sulphur (up to 90-95%) was established. The obtained sulphur concentrates contain 80-90% of elemental sulphur, which can be separated from sulphide residue through autoclave melting and settling. As a rule, sulphide concentrates remaining after extraction of sulphur contain up to 1-2% of noble metals. The sulphide concentrate can be purified to the level of rich concentrates or pure metals using the well-known methods as in the case of tankhouse slimes. The presented research specifies the parameters of main operations: pressure leaching and sulphur extraction. It was established that 98% of copper could be transferred into solution at temperatures of 108-110∞C and oxygen partial pressure 0.4-0.6 MPa. The above process may be realised as a one- or two-stage operation. Applying the two-stage operation will reduce the total residence time of the material in an autoclave and thus, the total number of required autoclaves. Experiments were carried out in autoclaves of various volumes using the products of nickel matte processing.

## Yazawa International Symposium on Metallurgical and Materials Processing: Principles and Technologies: Recycling, Waste Treatment and Environmental Issues II

*Sponsored by:* Extraction & Processing Division, EPD-Process Fundamentals Committee, EPD-Pyrometallurgy Committee, EPD-Aqueous Processing Committee, EPD-Copper, Nickel, Cobalt Committee, EPD-Lead and Zinc Committee, Jt. MPMD/EPD-Process Modeling Analysis & Control Committee; See Plenary Session for Co-Sponsors

*Program Organizers:* Hong Yong Sohn, University of Utah, Department of Metallurgical Engineering, Salt Lake City, UT 84112-0114 USA; Kimio Itagaki, Tohoku University, Institute for Advanced Materials, Sendai 980-8577 Japan; Florian Kongoli, FLOGEN Technologies, Inc., Materials Technology Department, Montreal, Quebec H3S 2CS Canada; Chikabumi Yamauchi, Nagoya University, Department of Materials Science & Engineering, Nagoya 464 8603 Japan

Tuesday AM — Room: Leucadia
March 4, 2003 — Location: San Diego Marriott Hotel

*Session Chairs:* Jes´s Contreras, Atlantic Copper S.A., Huelva Spain; Florian Kongoli, FLOGEN Technologies Inc., Matls. Tech. Dept., Montreal, Quebec H3S 2C3 Canada

TUESDAY AM

**8:30 AM Keynote**
**Metal Recycling and Waste Treatment**: *Yoshihiko Maeda*[1]; [1]Dowa Mining Company, Ltd., 1-8-2 Marunouchi, Chiyoda-Ku, Tokyo 100-8282 Japan

It is said that the 21st century will be an era to remedy global environment. To reserve natural resources for the future and to avoid dispersion of heavy metals, after usage, not to cause pollution problem, it is extremely important to recycle heavy metals as much as possible by reasonable recovery procedures. Nonferrous metal industry is expected to play a great role in recycling of heavy metals that are originally their products. From the depressed metal price experience in 1980th in Japan due to the sudden change in current exchange rate between US dollar and Japanese yen, one of major nonferrous metal company, Dowa Mining, has diversified its business area not only to so-called down stream, but also to environmental business including metal recycling, industrial waste treatment and soil remediation by utilizing technology and facilities once used or still used for mining and smelting of copper, zinc, lead and precious metals. In this paper, some of these applications will be presented.

**9:05 AM**
**The Decomposition Mechanism of Precursor 2,4,5-Trichlrorophenol for 2,3,7,8-TCDD Using Ab Initio Molecular Orbital Method Calculation**: *Takashi Araki*[1]; Mitsuhito Hirota[1]; Akio Fuwa[1]; [1]Waseda University, Grad. Sch. of Sci. & Eng., Ookubo 3-4-1 Soudai-rikou 60-110, Sinjuku-ku, Tokyo 169-8555 Japan

Dioxins (a generic term for PCDDs and PCDFs) have been the most serious air pollutants, because these compounds have highly acute and chronic toxicity. At present, removal and inhibition techniques of dioxins emission have been proposed by several workers, and catalytic decomposition method has been believed to be one of the most useful methods. However, the reaction mechanism on this method has not yet been clarified. In this work, we have paid attention to behavior of 2,4,5-trichlrorophenol, since this is the most generative precursor of 2,3,7,8-TCDD of the highest toxicity among PCDDs congeners. Such a study that clarifies the decomposition reaction mechanism of 2,4,5-trichlrorophenol may give us important knowledge for advancing the dioxin emission control. Thus, we have studied the decomposition mechanism of 2,4,5-trichlrorophenol using ab initio molecular orbital method calculation.

**9:30 AM**
**Scrap Combination for Recycling Valuable Metals: Direct Extraction and Recovery of Neodymium Metal from Magnet Scraps**: *Toru H. Okabe*[1]; Osamu Takeda[2]; Kazuhiro Fukuda[3]; Yoshiaki Umetsu[3]; [1]The University of Tokyo, Inst. of Industl. Sci., 4-6-1 Komaba, Meguro-ku, Tokyo 153-8505 Japan; [2]Santoku Company, Ltd., 4-14-34, Fukae-Kitamachi, Higashi-nada-ku, Kobe 658-0013 Japan; [3]Tohoku University, Inst. of Multidisciplinary Rsrch. for Adv. Matls. (IMRAM), 2-1-1 Katahira, Aoba-ku, Sendai 980-8577 Japan

A fundamental study was conducted with the purpose of establishing an environmentally sound recovery process for recycling valuable metals by combining scraps containing valuable metals. As an example, we investigated direct extraction and recovery of neodymium (Nd) in magnet scraps by utilizing liquid metal as an extraction agent. It was found that liquid magnesium (Mg) or silver (Ag) are suitable extraction agents, and can extract Nd out of iron alloys with high efficiency at around 1100 K. The newly developed extraction apparatus for Nd is a mechanically simple, static device without moving parts, where the Mg extraction medium circulates due to temperature difference inside the reaction vessel. This developed device can simultaneously accomplish continuous extraction of metal Nd from scraps, re-extraction of Mg from Mg-Nd alloy, and eventual recovery of pure Mg. As a result, metal Nd with 98% purity was directly recovered from magnet scraps under certain conditions. It was also shown that the extraction agent Mg could be reused. The results of this investigation show the possibility of establishing a procedure for directly extracting metal Nd in pure metal form without oxidization.

**9:55 AM**
**Distribution Behaviors in Recycling of Copper from the Waste**: *Junzo Hino*[1]; [1]Toho Tinanium Company, Ltd., Titanium Div., 3-3-5 Chigasaki, Chigasaki, Kanagawa-Pref. 253-8510 Japan

Most of the waste that contains a small portion of copper is landfilled. The recycling process of copper from the waste, such as shredder residue, should be developed in order to save mineral resources and prevent environmental pollution. Shredder residue generated from disposed automobiles and electric appliances consists of many types of plastics, glasses and metals. The combustion heat of plastics is efficiently used for melting in the recycling process, which consists of melting and reduction. The knowledge of distribution behaviors of main components is available to develop the process, because the waste contains a lot of different kind of components. Distribution behaviors in the recycling process are evaluated by using the thermodynamic calculation program, HSC Chemistry. The calculation results are compared with the practical operation data of the recycling process and discussed.

**10:20 AM Break**

**10:35 AM Invited**
**Environmental Policy and Continuous Improvement in Atlantic Copper**: *Jes´s Contreras*[1]; Adelino Alonso[1]; Pedro Hidalgo[1]; Miguel Palacios[1]; [1]Atlantic Copper S.A., Huelva 21001 Spain

Since the commencement of its activities in Huelva in 1970, Atlantic Copper has maintained a course of action that has been more demanding than the successive environmental legislations current at different times. As its primary objective it has sought compatibility between the protection of the environment and both its industrial activity and the social and economic development of the area in which its Metallurgical Complex is located. For this reason, since the seventies it has maintained a continuous programme of investments which have allowed it to attain its present environmental situation. As a consequence of the Environmental Policy of Atlantic Copper, in April 1998 it obtained certification for its Integrated System of Environmental Management (SIGMA) according to international standard ISO-14001, and under European Community Regulation 1836/93 for the Eco-Management and Eco-Audit System (EMAS). The SIGMA formalises the environmental management practices of Atlantic Copper and engages it to have available a system that can be fully audited. Atlantic Copper was the first European company in the non-ferrous metallurgical sector to obtain both the UNE-EN-ISO 14001 certification and the EMAS registration. The present paper reviews the actions by Atlantic Copper in environmental matters that have allowed it to achieve its present position. It also describes the coming stages of improvement planned and the modifications to be carried out in the near future, in particular the criteria for the selection of technologies on the basis of the concept of BAT (Best Available Techniques) introduced by the European Union, and always guided by the final objective of converting Atlantic Copper into a reference within the sector, comparable to the best designed and operated installations in the world.

**11:05 AM Invited**
**Phytoremediation Potential of Several Plants for Nickel Contaminated Soils**: *A. Cullaj*[1]; A. Hasko[2]; Florian Kongoli[3]; [1]University of Tirana, Dept. of Chem., Tirana Albania; [2]Agricultural University of Tirana, Dept. of Agronomy, Tirana Albania; [3]FLOGEN Technologies, Inc., 5757 Decelles Ave., Ste. 511, Montreal, Quebec H3S 2C3 Canada

Several industrial sites suffer from the contamination of soils from heavy metals, which are emitted among others by anthropogenic mining and metallurgical activities. Effective and economic physicochemical technologies for remediation of these sites remain elusive and costly. A new alternative remediation technique is the so-called phytoremediation. This is based on the ability of some plants to accumulate very high concentrations of metals from soils and thus providing the basis for a remediation of the contaminated sites. This technique, is an emerging branch of natural biotechnology and has several advantages compared to the sophisticated physicochemical techniques of soil remediation. It is not only environmentally friendly and pleasing to the eye but also its costs are quite low since it is solar driven, and, in some cases, plants can accumulate metals to such levels that economic mineral recovery maybe feasible even in conventional Ni refinery or smelting operations. In this work, the potential of many plants to accumulate nickel has been investigated in order to identify the species which offer the best phytoremedial potential for nickel contaminated soils. Field surveys have been made in five nickel-containing sites in order to identify the nickel tolerant species that have spontaneously grown in contaminated soils. Atomic Absorption Spectrometry measurements were carried out on 145 different plants collected. 16 of them were identified as having an hyper ability to accumulate nickel since they contained more than 10 000 mg Ni per kg (DW). Seven taxa are of Alyssum genus and one of Bornmuellera genus of Cruciferae. The highest accumulation of nickel was present in aerial parts of Alyssum murale var. chlorocarpum Hausskn (25 500 mg/kg) and Alyssum markgrafii O.E. Schulz (23 700 mg/kg). The seeds germinated are more evidenced at A.m.var. chlorocarpum, about 63%. These plants are suggested as the most promising species to be used for phytoremediation purposes in nickel contaminated soils.

**11:35 AM**

**Development of Roasting Process for Fly Ash from Municipal Incinerators**: *Mototsugu Matsuno*[1]; Katsuhiro Tomoda[1]; Junnichi Takahashi[1]; [1]Sumitomo Metal Mining Company, Ltd., Energy & Environ. Business Div., 5-11-3 Shinbashi Minato, Tokyo 105-8716 Japan

Several types of process have been developed for treating fly ash generated from municipal incinerators. The incinerator fly ash contains not only toxic metals such as lead and cadmium, but also dioxins. A new process was examined in the present study. Fly ash is formed into green pellets with some additives, and the pellets are then roasted to eliminate or stabilize the toxic metals, and to decompose dioxins. The roasted pellets become harmless through this process, and are recycled as artificial lightweight aggregates. Volatilized metals are collected as secondary fly ash, and recovered at non-ferrous smelting plants. A new pilot plant of this process, with a capacity of approximately 100 kg/hr, was installed and several types of test were carried out. The characteristics of this process technology are complete reduction of heavy metals, strict stabilization of residual metals and high-strengthen pellets production by sintering. Mechanism of roasting is also analysed.

## Yazawa International Symposium on Metallurgical and Materials Processing: Principles and Technologies: Advances in Non-Ferrous Production Technologies and Industrial Practice: Lead-Zinc

*Sponsored by:* Extraction & Processing Division, EPD-Process Fundamentals Committee, EPD-Pyrometallurgy Committee, EPD-Aqueous Processing Committee, EPD-Copper, Nickel, Cobalt Committee, EPD-Lead and Zinc Committee, Jt. MPMD/EPD-Process Modeling Analysis & Control Committee; See Plenary Session for Co-Sponsors

*Program Organizers:* Hong Yong Sohn, University of Utah, Department of Metallurgical Engineering, Salt Lake City, UT 84112-0114 USA; Kimio Itagaki, Tohoku University, Institute for Advanced Materials, Sendai 980-8577 Japan; Florian Kongoli, FLOGEN Technologies, Inc., Materials Technology Department, Montreal, Quebec H3S 2CS Canada; Chikabumi Yamauchi, Nagoya University, Department of Materials Science & Engineering, Nagoya 464 8603 Japan

Tuesday AM — Room: Santa Rosa
March 4, 2003 — Location: San Diego Marriott Hotel

*Session Chairs:* Yong Hack Lee, Korea Zinc Company Ltd., Seoul Korea; Andreas Siegmund, RSR Technologies Inc., Dallas, TX 75207 USA

**8:30 AM Keynote**

**Modern Applied Technologies for Primary Lead Smelting at the Beginning of the 21th Century**: *Andreas Siegmund*[1]; [1]RSR Technologies, Inc., 2777 Stemmons Freeway, Ste. 1800, Dallas, TX 75207 USA

During the decade of the nineties the conventional method of primary lead smelting (sinter machine/blast furnace) was successfully challenged by the introduction of novel direct and continuous smelting processes. These modern technological innovations like the QSL, Kivcet, and Isa/Ausmelt process, became more than major competitors and in combination with a significant shift in market structure as well as more stringent government regulations, caused radical changes in many different aspects. They have proven to be economically and environmentally viable. The intensification of the metallurgical reaction by applying the bath or flash smelting principle in conjunction with the usage of oxygen resulted in cost savings and a higher flexibility with respect to raw materials and additives usage. By synchronizing individual auxiliary plant sections with the smelting process nearly optimum energy exploitation, a virtually waste-free production and low-emission mode of operation is achieved. The primary lead industry is at a crossroad where novel high-energy efficient technologies will gradually substitute the sinter-blast furnace operation in the new millennium.

**9:05 AM**

**Thermodynamic Study on Recovery of Lead and Antimony from a Used Lead-Battery**: *Satoshi Itoh*[1]; Atsushi Kikuchi[1]; Mitsuhisa Hino[2]; [1]Tohoku University, Grad. Sch. of Eng., Dept. of Metall., Aramaki-Aza-Aoba 02, Aoba-ku, Sendai 980-8579 Japan; [2]Tohoku University, Inst. of Multidisciplinary Rsrch. for Adv. Matls., Katahira, Aoba-ku, Sendai 980-8577 Japan

Phase equilibria and activities of the components in the liquid lead-antimony-oxygen ternary system, which is of fundamental importance for discussing the recovery of lead and antimony from a used lead-battery, have been investigated at 1173 and 1223 K. The two liquid phases of metal and oxide were observed at the temperatures studied, and the tie lines indicating isoactivities were determined. The activities of PbO, SbO1.5 and Sb2O3 in the PbO-SbO1.5 and PbO-Sb2O3 pseudo-binary systems were then obtained by applying the Gibbs-Duhem equation to the phase relation of metal-oxide equilibrium. Both in the pseudo-binary systems the activities exhibit negative deviations from Raoultís law. The vapor pressures of lead, antimony and lead oxide, antimony oxide were calculated by using the activities of the components in the lead-antimony-oxygen ternary system. As a result, an oxidation of antimony concentrated in an anode slime followed by evaporation as antimony oxide Sb4O6 was found to be considerably effective for the recovery of lead and antimony from a used lead-battery.

**9:30 AM Invited**

**Simulation of Imperial Smelting Furnace Operation Using a Mathematical Model**: *Kenji Matsuzaki*[1]; Fumio Tanno[2]; Akio Fuwa[3]; [1]Mitsui Mining & Smelting Company, Ltd., Corporate R&D Ctr., 1333-2 Haraichi, Ageo-shi, Saitama 362-0021 Japan; [2]Metal Economics Research Institute, Japan, 2-6-4 Toranomon, Minato-ku, Tokyo 105-0001 Japan; [3]Waseda University, Dept. of Matls. Sci. & Eng., 3-4-1 Ohkubo, Shinjuku-ku, Tokyo 169-8555 Japan

A mathematical simulation model of the Imperial Smelting Furnace Operation has been developed to clarify the internal state of the furnace and to improve the furnace operation. The model consists of top, shaft and bottom regions. Analysis in the shaft region is based on differential heat and materials balances taking account of reaction kinetics and heat transfer rate, and those in the top and the bottom regions are based on heat and mass balances under steady state condition. Longitudinal distributions of process variables such as temperatures of gas, sinter and coke, gas composition and reaction extend under a practical operating condition are then calculated. The ISF performance under various operating conditions has also been estimated. A new process for zinc smelting has also been proposed and analyzed using this model.

**10:00 AM**

**The Nature of Accretion Formation During Roasting of Zinc Concentrates in Fluidized Bed Furnace**: *N. M. Komkov*[1]; V. A. Luganov[2]; [1]D. Serikbaev East-Kazakhstan Technical University, 19 Serikbayev Str., Ust-Kamenogorsk 492010 Kazakhstan; [2]K. Satpaev Kazakh National Technical University, 22 Satpaev Str., Almaty 480013 Kazakhstan

The main operation of obtaining zinc from sulfide raw materials by hydrometallurgical technology is oxidizing roasting of zinc concentrates in fluidized bed furnaces. The technical-economic parameters are determined by the parameters of the roasting process which in their term depend on the composition of initial raw materials, the temperature of the bed and on other factors. Keeping up of the predetermined temperature of roasting is due to the change of specific efficiency as well as to quantity of heat removed from the bed. The efficiency the caissons depends in a high degree on the composition and thickness of the accretion formed on the surface of the caissons. Forecasting the roasting results is impossible unless we know the accretion formation mechanism. The aim of the present paper is the thermodynamic analyses of behavior of the charge compositions under roasting and determination of the potential mechanism accretion formation. The thermodynamic analyses show that under conditions of oxidizing roasting the thermodynamic probability of zinc sulfate formation is higher than the probability of oxide formation till temperature of 873 K is reached. The thermodynamic probability of lead sulfate formation is higher than the probability of oxide formation in the whole temperature range of roasting. The probability of formation of ferrites and silicates of zinc only insignificantly decreases the sulfate stability. The results of investigation of accretion composition formed under roasting of concentrates with the particle size less than 0.02 mm (60%), containing 65% of sphalerite (ZnS), 12% of pyrite and chalcopyrite ($FeS_2$ and $CuFeS_2$) each, 3% of galenite (PbS), 7% of silica and other non-ore minerals, have shown the following. The composition of accretion varies depending on the depth of the accretion layer. The accretions on the caissons and the thermo-siphons consist mostly of zinc sulfate (more than 50%). The accretions of forchamber consist mostly of zinc oxide. They also contain ferrites and silicates. Formation of sulfate zinc accretion on cold parts of fluidized bed furnace (on the caissons and on the thermo-siphons) may be explained by a lower temperature on the surface and probably by catalytic influence of oxides present at caissons and thermo-siphons surface on the formation of $SO_2$ and sulfates. The nature of the accretion structure on the hotter parts of the furnace may supposedly be explained by formation of elemental vaporous zinc during roasting.



**10:25 AM Break**

**10:35 AM Keynote**

**The Experience of Lead Direct Smelting in Korea Zincís Onsan Refinery**: *Yong Hack Lee*[1]; Young Min Park[1]; [1]Korea Zinc Company, Ltd., 142 Nonhyon-dong Kangnam-Ku, Seoul 135-749 Korea

Nonferrous smelting processes have been rapidly changed since the beginning of 1980. The copper smelting technology has been changed to the Flash Smelting and MIB process from the conventional Blast Furnace process. In the field of lead smelting, the technology has changed from Blast Furnace Smelting to the Direct Smelting such as QSL and KIVCET. At 1992, Onsan Refinery of Korea Zinc successfully commissioned Direct Smelting QSL technology for lead. The QSL can produce more than 160,000 ton per year of lead bullion from lead concentrate and various scraps. Moreover, since 2000, the TSL (Top Submerged Lance) Technology utilizing the same Direct Smelting process has been successfully commissioned to treat low grade of lead concentrate as well as lead sulfate residue produced from a hydrometallurgical zinc plant. This paper presents and compares the energy flows of lead smelting processes such as a conventional process and the Direct Smelting Processes plotted on the Pb-O-S phase diagram. The differences of enthalpy and free energy change are also discussed based on the each smelting path. The potential diagram of $CO/CO_2$ suggests how to control the oxygen potential in furnace. Also, it describes the recent operational experience in TSL plant of Onsan Refinery with necessary mass balance of key elements.

**11:10 AM Invited**

**Direct Production of Metallic Zinc from EAF Dust**: *Takeshi Azakami*[1]; Hirofumi Sugimoto[2]; Sachio Kojima[2]; [1]Saitama Institute of Technology, Grad. Sch. of Eng., Okabe, Saitama 369-0293 Japan; [2]Sotetsu Metal Company, Ltd., Bandai 1414, Bandai, Fukushima 969-3301 Japan

In Japan, more than 500 thousand tons of EAF dust is generated every year. Zinc source in the dust reaches 17 to 25% of annual zinc production in Japan. Most of this zinc in EAF dust has been recovered as crude zinc oxide by carbon reduction in rotary kilns or other furnaces. Produced crude zinc oxide is valued very cheap because it has to be treated again as a raw material of zinc pyrometallurgy. With the view of direct production of metallic zinc, fundamental experiments were carried out by applying ìIron Reduction Vaporization Methodî. The purpose of the study is to cut down the treatment costs and to make more profit on dust treatment process. Also, by this process, decreasing in $CO_2$ generation would be attainable. By larger scale tests, zinc ingots have been produced, and industrialization of the process will be hopefully expected.

**11:40 AM**

**Installation of Arsenic Removal into the Hematite Process**: Hitoshi Msauda[1]; Shigeki Sato[1]; Yoshito Kudo[1]; *Yutaka Shibachi*[1]; [1]Akita Zinc Company, Ltd., Hematite, 217-9 Shimo-Kawabata Furumichi Iijima, Akita 011-0911 Japan

The Iijima Zinc Refinery started operation in 1972, and has an annual capacity of 200,000t-Zn today. The hematite process was employed for the first time and we have been pursuing the ideal of waste-free refinery for 30 years. In recent years, however, only a half of the hematite produced could be sold to the cement industry and reducing arsenic level had been anticipated for selling them all. The arsenic cementation process with zinc powder, which was developed in the long time laboratory works, was determined best for hematite process among some options. The construction works started in 2000 and was put into operation in 2001, and all hematite were sold to the cement industry in the same year. The outline of this project, present operation and technical issue will be reported in this paper.

## Yazawa International Symposium on Metallurgical and Materials Processing: Principles and Technologies: Advances in Non-Ferrous Production Technologies and Industrial Practice: General II

*Sponsored by:* Extraction & Processing Division, EPD-Process Fundamentals Committee, EPD-Pyrometallurgy Committee, EPD-Aqueous Processing Committee, EPD-Copper, Nickel, Cobalt Committee, EPD-Lead and Zinc Committee, Jt. MPMD/EPD-Process Modeling Analysis & Control Committee; See Plenary Session for Co-Sponsors

*Program Organizers:* Hong Yong Sohn, University of Utah, Department of Metallurgical Engineering, Salt Lake City, UT 84112-0114 USA; Kimio Itagaki, Tohoku University, Institute for Advanced Materials, Sendai 980-8577 Japan; Florian Kongoli, FLOGEN Technologies, Inc., Materials Technology Department, Montreal, Quebec H3S 2CS Canada; Chikabumi Yamauchi, Nagoya University, Department of Materials Science & Engineering, Nagoya 464 8603 Japan

Tuesday AM — Room: Point Loma
March 4, 2003 — Location: San Diego Marriott Hotel

*Session Chairs:* Ramana G. Reddy, The University of Alabama, Dept. of Metallurgl. & Matls. Eng., Tuscaloosa, AL 35487-0202 USA; Brajendra Mishra, Colorado School of Mines, Metallurgl. & Matls. Eng., Golden, CO 80401 USA

**8:30 AM Keynote**

**Application of Molten Salts in Metals Production**: *Brajendra Mishra*[1]; [1]Colorado School of Mines, Metallurgl. & Matls. Eng., 1500 Illinois St., Golden, CO 80401 USA

Molten Salt electrolytic processes offer unique opportunities to extract and refine metals where gaseous or metallothermic reduction, hydrometallurgical extraction and aqueous electrolytic methods are thermodynamically constrained. Production of aluminum and magnesium by molten salt electrolysis are well known commercial processes. Several other reactive metals, such as lanthanides and actinides, as well as beryllium and calcium, make use of molten salt processing for extraction and refining. This presentation describes the science of molten salt chemistry and electrochemistry for winning and refining of several metals. In addition, recovery of metals from waste process salts by molten salt reduction as well as oxidation have been discussed. Material issues in design of molten salt reactors have been included. Various applications have been presented through case studies. Experimental data have been included to justify the suitability as well as limitations of these specific processes.

**9:05 AM**

**Thermogravimetric Study of the Sulfurization of $TiO_2$ Using $CS_2$ and $H_2S$**: *Nobuaki Sato*[1]; Jhon Cuya[1]; Katsutoshi Yamamoto[1]; Atsushi Muramatsu[1]; [1]Tohoku University, Inst. of Multidisciplinary Rsrch. for Adv. Matls., 2-1-1 Katahira, Aoba-ku, Sendai 980-8577 Japan

Titanium dioxide is the well-known catalyst for the photodecomposition of water in uv region. On the other hand, titanium sulfides absorb the visible light, though it is rather unstable in water because of its photo-dissolution. In this regard, partially sulfurized $TiO_2$ is expected to be chemically stable and have an enhanced photocatalytic activity compared with $TiO_2$. For the analysis of sulfurization behavior of TiO2, thermogravimetric study on the sulfurization of TiO2 was made using a thermo-balance with a quartz spring. In the case of CS2, sulfurization reaction started at around 773 K with heating rate of 1 K/min. The weight increase curve showed a maximum of c.a. 30 wt% at around 1023 K and then gradually decreased to c.a.12 wt% at 1273 K. This would be caused by the formation of TiS2 followed by the decomposition of TiS2 to lower sulfides. The sulfurization behavior of TiO2 using H2S was also investigated compared with that of CS2.

**9:30 AM**

**Decomposition of Sulfide Concentrates Under Concentrated Solar RadiationñA Novel Approach to Effect the Direct Decomposition of Sulfides**: Lenny Winkel[1]; Christine Guesdon[1]; *Marcel Sturzenegger*[1]; [1]Paul Scherrer Institut, High-Temp. Solartech., OVGA/103A, Villigen PSI 5232 Switzerland

The decreasing demand for sulfuric acid as well as attempts to reduce $CO_2$ emissions stimulated research activities aiming at new process routes for metal extraction. The most intriguing approach to avoid formation of sulfur dioxide ($SO_2$) and that of intermediate oxides is the direct conversion of metal sulfides into the metal and elemental sulfur. A promising path to realize the direct conversion is the use of concentrated solar radiation. Thermodynamic calculations suggest that many non-ferrous metal sulfides decompose into the metal and sulfur at temperatures between 1300 and 2000°C. Such temperatures are readily accessible in solar chemical reactors and metal extraction with high maximum efficiencies and reduced or zero emission of $SO_2$ and $CO_2$ can be envisioned. Experimental work on solar metal extraction has been initiated for zinc and copper. Chemical reactivity studies by means of thermogravimetry and powder x-ray diffractometry have shown that extraction of copper is easier to effect than that of zinc: During the decomposition of copper sulfides gaseous sulfur naturally separates from liquid copper, while decomposition of zinc sulfide generates a vapor with zinc and sulfur being mixed. To prevent zinc and sulfur from reacting back to the parent zinc sulfide, additional measures, e.g. fast cooling, are required. Chemical equilibrium calculations have confirmed that the solar decomposition of copper sulfide concentrates provides an additional benefit with regard to removal of volatile impurities. Since the solar decomposition can be conducted in absence of oxygen, slag forming reactions will be suppressed and impurities such as arsenic or antimony can easily be separated from copper metal by evaporation. After a short description of the novel approach the paper will firstly report on the chemical equilibrium calculations carried out for evaluating the potential of impurity removal and secondly present an imaging furnace, set up for studying the decomposition of sulfides at temperatures up to 2000°C.

**9:55 AM**

**Removal of Boron from Metallurgical-Grade Silicon by Applying CaO-Based Flux Treatment**: *Mitsuru Tanahashi*[1]; Hideo Nakahigashi[1]; Kunihiko Takeda[1]; Chikabumi Yamauchi[2]; [1]Nagoya University, Dept. of Matls. Sci. & Eng., Grad. Sch. of Eng., Furo-cho, Chikusa-ku, Nagoya, Aichi 464-8603 Japan; [2]Chubu University, Dept. of Mechl. Eng., Sch. of Eng., 1200 Matsumoto-cho, Kasugai, Aichi 487-8501 Japan

In order to develop economical production process from metallurgical-grade silicon (MG-Si) to solar-grade (SOG-Si), removal behavior of boron from molten MG-Si was investigated at 1773 K by two following CaO-based flux treatment processes, which can establish special condition of both high basicity of flux and high oxygen partial pressure at boron removal reaction sites: [1] Boron removal from MG-Si by flux addition onto the molten silicon followed by oxygen gas injection into the melt (Two-stage connecting process). [2] Boron removal from MG-Si by simultaneous injection of flux powders and oxygen gas into the molten silicon (Simultaneous injection process). By these treatment processes, especially simultaneous injection process using a flux powder injection equipment, boron content in MG-Si can be reduced efficiently. Based on the results obtained, optimum conditions for boron removal by the flux treatment were examined from the viewpoints of operating time, oxygen gas flow rate, and so on.

**10:20 AM Break**

**10:40 AM**

**Sulfur and Oxygen Potential Ratios Prediction in Copper Flash Smelting Plants Using Reddy-Blander Model**: *Bora Derin*[1]; Ramana G. Reddy[1]; [1]Istanbul Technical University, Dept. of Metallurgl. & Matls. Eng., Istanbul 80626 Turkey; [1]The University of Alabama, Dept. of Metallurgl. & Matls. Eng., Tuscaloosa, AL 35487-0202 USA

In smelting furnace conditions, copper losses in liquid fayalitic slags are both as entrained matte and as chemically dissolved species. Using Reddy-Blander (RB) model, the entrained sulfur content in the slags and the exact potential ratios of sulfur and oxygen for several copper flash smelting plants were derived. The sulfide capacities (Cs) of six different flash smelting plants multicomponent ($FeO-CuO_{0.5}-CaO-MgO-FeO_{1.5}-AlO_{1.5}-SiO_2$) slags were calculated. The log ($PO_2PS_2$) versus matte grades of the industrial furnaces was determined. The $PO_2PS_2$ratio increases with an increase of copper grade and for the copper flash smelting condition, the calculated $PO_2PS_2$ ratios were found to be in very good agreement with the experimental and plant data. Hence, the RB Model predicted that sulfide capacity could be calculated a priori, based on a simple solution model and on knowledge of the chemical and solution properties of sulfides and oxides.

**11:05 AM Invited**

**Roasting Mechanisms of Impure Zinc Concentrates in Fluidised Bed**: Maija-Leena Mets‰rinta[1]; *Pekka A. Taskinen*[1]; Satu K. Jyrkˆnen[1]; Aija Rytioja[2]; Jens Nyberg[2]; [1]Outokumpu Research, PO Box 60, Pori 28101 Finland; [2]Outokumpu Zinc, PO Box 26, Kokkola FIN-67101 Finland

The behaviour of copper and lead in zinc roasting has been studied in laboratory scale roasting and large scale trials in an industrial fluidized bed, with the background of Outokumpu Kokkola Zinc smelter. Commercial zinc concentrates with a low and high ( up to 3 wt % ) copper content and with a low and high ( up to 3.5 wt % ) lead content were oxidized to various desulphurisation degrees in the fluidised bed to establish the reaction mechanisms and the paths for copper and lead oxidation in the roasting. Influences of the agglomerate size on the roasting kinetics and micro-scale phenomena were also determined. Optical microscopy was used on the calcine and the findings are presented as numerous photographs of the polished cross sections. SEM/EDS techniques were used for analyzing chemically the phases and particle morphologies present in the samples. Computational thermodynamics was applied to the complex phase equilibria occurring during roasting in the agglomerating calcine. A complete oxidation of zinc concentrate with a high copper and lead content requires a careful control of oxygen coefficient in the roasting in order to maintain a stable operation of the fluidised bed. Oxygen coefficient thus seems to have a significant impact on the hydrodynamic stability of the fluidized bed with fine raw materials.

**11:30 AM Invited**

**Some Aspects of Cleaning of Ni, Co and Cu-Containing Slags Via Oxide Melt Blowing by Reducing Gases**: *L. Sh. Tsemekhman*[1]; A. G. Ryabko[1]; L. B. Tsymbulov[1]; M. V. Knyazev[1]; V. B. Fomichev[1]; A. A. Ryumin[1]; L. A. Pavlinova[1]; [1]AO ìGipronickelî, 1 Grazhdansky Pr., Saint-Petersburg 195220 Russia

One of the methods of cleaning slags containing Ni, Co, and Cu is their blowing by reducing gas mixtures formed in the process of gas or liquid fuel firing. The investigations carried out by us have shown that the acceptable residual Ni and Co content is achieved by means of natural gas combustion at a<0,7 and solid reducer consumption at the level of 6-10%. The values of cleaning are independent of gas-solid fuel consumption ratio and determined by partial oxygen pressure achieved during both fuels oxidizing. The results obtained from cleaning of industrial slags of different compositions by gas mixtures corresponding by composition to various conditions of natural gas combustion are given in the report. The influence of introduced sulphur-containing collector on the cleaning values, as well as the importance of interaction of produced alloys, mattes, slags, and a gas phase are considered.

## Actinide Materials: Processing, Characterization, and Behavior: Advanced Fuel Cycles

*Sponsored by:* Light Metals Division, Structural Materials Division, ASM International: Materials Science Critical Technology Sector, SMD-Nuclear Materials Committee-(Jt. ASM-MSCTS), LMD-Reactive Metals Committee

*Program Organizers:* Sean M. McDeavitt, Argonne National Laboratory, Chemical Technology Division Materials Development Section, Argonne, IL 60439-4837 USA; Michael F. Stevens, Los Alamos National Laboratory, Los Alamos, NM 87545 USA

Tuesday PM Room: 4
March 4, 2003 Location: San Diego Convention Center

*Session Chair:* David Senor, Pacific Northwest National Laboratory, Richland, WA 99352 USA

**2:00 PM Keynote**

**An Overview of Actinide Processing: Chemical Separations Methods for Recycle and Transmutation**: *James J. Laidler*[1]; [1]Argonne National Laboratory, Chem. Tech. Div., 9700 S. Cass Ave., Bldg. 205, Argonne, IL 60439-4837 USA

Commercial nuclear power reactors in the United States presently generate about 2,000 tons of spent fuel each year. At this rate, the accumulated spent fuel in temporary storage at reactor sites will exceed the legislated capacity of the recently-approved Yucca Mountain Repository almost as soon as the repository is opened for spent fuel disposal. The need for a second repository can be precluded by a system of selective chemical separations that partition the spent fuel into (1) a comparatively large mass of uranium that can be disposed cheaply or recycled, (2) transuranic elements that can be recycled into advanced reactors for recovery of their energy value, (3) short-lived fission products with high heat generation rates that can be stored inexpensively until they decay completely, and (4) a relatively small mass of other fission products that must be stored in a high-level waste repository. The separations methods to accomplish this partitioning are presently under development in the United States.

**2:40 PM**

**Electrochemical Reduction of Spent Oxide Fuel**: *Karthick Gourishankar*[1]; Lazlo Reedy[1]; Diane Graziano[1]; [1]Argonne National Laboratory, Chem. Tech. Div., 9700 S. Cass Ave., Argonne, IL 60439-4837 USA

Argonne National Laboratory (ANL) has developed a direct electrochemical reduction process for converting oxides to metals with application in the recovery of actinides from spent oxide fuels. The major components of the electrochemical cell are: (1) a molten-salt electrolyte, (2) an oxygen-evolving electrode, (3) a cathode at which solid oxides are reduced, and (4) a reference electrode for monitoring and controlling cell operations. The reduction occurs by a solid-state electrochemical transformation without the need for dissolution of the feed oxide in the electrolyte. Complete reduction of UO2 has been demonstrated using a platinum anode. Our work with UO2 has led to an improved understanding of the reduction mechanism and the parameters affecting the process rate. Bench-scale experiments have been initiated to develop the process for reduction of the transuranic and rare-earth oxides that are present in the spent oxide fuel. In this paper, we will present and discuss results from our recent bench-scale experiments.

**3:00 PM**

**Direct Preparation of Niobium Based Superconducting Alloys by Electro-Deoxidation of the Oxides**: Xiao Y. Yan[1]; *Derek J. Fray*[1]; [1]University of Cambridge, Matls. Sci. & Metall., Pembroke St., Cambridge CB2 3QZ UK

Niobium based superconductors, Nb, NbTi and Nb3Sn are usually made from the powders of the metallic elements that are expensive and relatively difficult to prepare in the low oxygen form. Electro-deoxidation consists of starting with an intimate mixture of the oxides and making compacted mixture the cathode in a bath of fused calcium chloride and sodium chloride. On the application of a potential below the decomposition potential of calcium chloride, the cathodic reaction is the ionisation of oxygen and its subsequent transfer to the anode as oxygen ions, dissolved in the melt. The metallic product was found to be an alloy or intermetallic compound of the two elements whose superconducting properties were identical to those reported in the literature.

**3:20 PM**

**Recent Advances in Uranium High Throughput Electrorefining**: *James L. Willit*[1]; G. A. Fletcher[1]; R. J. Blaskovitz[1]; J. Figueroa[1]; M. A. Williamson[1]; [1]Argonne National Laboratory, Chem. Tech. Div, 9700 S. Cass Ave., Bldg. 205, Argonne, IL 60439-4837 USA

Uranium electrorefining lies at the heart of an electrometallurgical treatment process for spent metallic reactor fuel. The challenges in developing a device that can efficiently electrorefine several tons of uranium per year are in the engineering of the device, not in the fundamental electrochemistry. The fundamental electrochemistry of uranium electrorefining in a molten chloride salt has been understood since the 1950ís. Over the past seven years, we have tested various uranium electrorefiners with capacities ranging from a few kilograms to 150 kilograms. One device, the Mk-V electrorefiner, has been installed in the Fuel Conditioning Facility at Argonne-West and is presently being used to treat spent EBR-II blanket fuel. Results from recent tests that focus on a new anode geometry and the improvement in efficiency arising from a third set of electrodes in the cell will be presented.

**3:40 PM Break**

**4:00 PM**

**Pyrochemical Separations of TRU and Fission Product Content from Metal Alloy Fuels**: *Michael K. Richmann*[1]; William E. Miller[1]; Zygmunt Tomczuk[1]; Diane J. Graziano[1]; [1]Argonne National Laboratory, Chem. Tech. Div., Bldg. 205, 9700 S. Cass Ave., Argonne, IL 60439 USA

A primary goal of the U.S. Advanced Accelerator Applications (AAA) program is the provision of an alternative to the direct disposition of commercial spent nuclear fuel in a repository. This is achieved by converting the transuranic elements and long-lived fission products in this waste to stable or short-lived fission products. A head-end step (UREX) is used to separate the uranium, technetium and iodine from the transuranics (TRU) and other fission products in commercial spent LWR fuel. Pyro-A, a pyrochemical process, is used to partition the transuranics from the fission products to form a transmuter blanket fuel that is a zirconium/plutonium metal alloy. This is accomplished by an oxide-reduction step to metal on the UREX product followed by an electrorefining step to recover the TRU content from the fission products prior to alloy fuel fabrication. We will present data for the Pyro-A process electrorefining experimentation demonstrating the kinetics and degree of TRU recovery.

**4:20 PM**

**Processing Experiences During the Electrometallurgical Treatment of Spent Nuclear Fuel**: *Brian R. Westphal*[1]; [1]Argonne National Laboratory, PO Box 2528, Idaho Falls, ID 83403 USA

An electrometallurgical process is currently being developed by Argonne National Laboratory for the treatment of spent nuclear fuel. Sodium-bonded spent nuclear fuel is being processed in a hot cell environment as a demonstration of applicability for the technology to other types of spent fuel. During the process development program, optimal operating conditions for the equipment are being investigated with respect to throughput, product purity, and recovery. A steady increase in the current processing rates to a production level allows for the continual development of the process. Although as yet undetermined, the disposition of the final uranium products will be based on the contribution of impurities, primarily plutonium, to the product. Recovery of the uranium during processing is influenced by both throughput requirements and the secondary waste streams. The results and experiences from the development program will be discussed as well as challenges encountered and their resolution.

**4:40 PM**

**Electrochemical Investigation of the Uranium Exchange Current Density in LiCl-KCl Eutetic**: *Valerie Goss*[1]; K. V. Gourishankar[1]; J. L. Willit[1]; [1]Argonne National Laboratory, Chem. Tech. Div., 9700 S. Cass Ave., Bldg. 205, Argonne, IL 60439-4837 USA

The exchange current density (ECD) of uranium has not been adequately documented under various experimental conditions and fuel types. In this study, electrochemical methods were used to measure the ECD of depleted uranium metal in a molten LiCl-KCl salt solution. The experimental set-up included a direct power source, a uranium foil cathode, and a uranium strip as the anode. The electrolyte employed was a LiCl-KCl-UCl3 eutetic molten salt. UCl3 concentrations were 1.36- and 1.83-weight %, and reactions were performed at 450-, 500-, and 550-K inside a helium glovebox. In the electrochemical cell, small currents were applied, and overpotentials were recorded. The open-circuit potentials ranged from 0.1- to 0.4-mV. The experimental data indicates that the exchange current density is approximately 50 mA/cm2 suggesting that electrode reactions involving uranium may not be as fast as previously expected.

**5:00 PM**
**Electrochemical Deoxidation of CaO in a CaO-CaCl2 Melt with a Solid Oxide Membrane**: David Lambertin[1]; Laurent Pescayre[1]; Gilles BourgËs[1]; Alice Martin[3]; Michel P. Allibert[2]; Jacques Fouletier[3]; Jean-Claude Poignet[3]; [1]CEA/Valduc, DTMN/SRPU, Centre díÈtudes de Valduc, Is Sur Tille 21120 France; [2]Ecole Nationale SupÈrieure díElectrochimie et díElectromÈtallurgie de Grenoble (Groupe INPG), LTPCM, 1130 Rue de la piscine, BP 75, Saint Martin díHËres 38402 France; [3]Ecole Nationale SupÈrieure díElectrochimie et díElectromÈtallurgie de Grenoble (Groupe INPG), LEPMI, 1130 Rue de la piscine, BP 75, Saint Martin díHËres 38402 France

Oxide reduction by calcium metal in a CaCl2 melt produces metal and calcium oxide (CaO), dissolved in the molten chloride. In order to minimize waste salts, the reacted salts have to be regenerated. It can be done (i) by converting CaO to CaCl2 by chlorination with Cl2 and adding calcium metal or (ii) by the electrochemical deoxidation of CaO (reduction of Ca2+ to Ca and oxidation of O2- to O2). In the first method, the addition of calcium metal increases the amount of reacted salts, and consequently the waste salts, while in the second method the quantity of reacted salts is constant. Finally the electrochemical deoxidation of CaO occurs in one step and the produced oxygen is evacuated. The experimental set up comprised a magnesia crucible containing a CaO-CaCl2 melt at 830∞C, in which was dipped an iron cathode and an yttria-stabilized zirconia tube. The anode was the platinized inner wall of the zirconia tube. A current density of 50 mA/cm≤ with a potential difference of 6 V has been applied during 24 hours. The current efficiency for oxygen production was close to 100%.

## Alumina and Bauxite: Bauxite and Alumina Extraction

*Sponsored by:* Light Metals Division, LMD-Aluminum Committee
*Program Organizers:* David Kirkpatrick, Kaiser Aluminum & Chemical Group, Gramercy, LA 70052-3370 USA; Steve Rosenberg, Worsley Alumina Pty, Ltd., Process Chemistry Group, Collie, West Australia 6225 Australia; Paul Crepeau, General Motors Corporation, MC/486-710-251, Pontiac, MI 48340-2920 USA

Tuesday PM — Room: 3
March 4, 2003 — Location: San Diego Convention Center

*Session Chairs:* David Kirkpatrick, Kaiser Aluminum & Chemical Group, Gramercy, LA 70052-3370 USA; Steve Rosenberg, Worsley Alumina Pty Ltd., Process Chem. Grp., Collie, W. Australia 6225 Australia

**2:00 PM Introductions**

**2:10 PM**
**Recent Innovations in Controlling Fugitive Dust Emissions in the Bauxite/Alumina Industry**: *D. Casey Roe*[1]; [1]General Electric, GE Betz, 4636 Somerton Rd., Trevose, PA 19053 USA

Fugitive dust emissions are becoming a growing Global concern. In the bauxite/alumina industry, dust emissions are generated during the mining, transport and handling of bauxite, and in red mud disposal areas. While environmental, health and safety issues are the primary reasons for concern, dust can also have a major economic impact on an operation, e.g., increased maintenance and clean-up costs, and the loss of bauxite prior to digestion. While water can minimize certain dust problems, the results are short-term, and water addition can cause wet bauxite handling problems and increased transportation costs. This paper summarizes recent innovations for reducing dust emissions from bauxite mines to red mud disposal areas. Examples include a method for controlling dust during mining operations, automated equipment and chemicals for controlling bauxite dust, road and surface stabilization, and red mud disposal area dust control.

**2:40 PM**
**Improvements of the Processes to Produce Alumina from Chinese Diasporic Bauxite**: *Songqing Gu*[1]; *Zhongling Yin*[1]; [1]Zhengzhou Light Metal Research Institute, No. 82 Jiyuan Rd., Shangjie Dist., Zhengzhou, Henan Province 450041 China

In this paper the characteristics of Chinese diasporic bauxite resource and its main behaviors in the alumina production are analysed. The important aspects of the processes and technology applied in Chinese alumina industry including Bayer process, sintering process and combined process are presented. The potential and direction of technology development of Chinese alumina industry are discussed.

**3:10 PM**
**Investigation on the New Digesting Process of Diaspore**: *Zhao Qingjie*[1]; *Yang Qiaofang*[1]; Qi Lijuan[1]; [1]Aluminium Corporation of China, Ltd., Zhengzhou Rsrch. Inst., Zhengzhou, Henan 450041 China

Based on the extensive study on the reaction behaviors and digesting kinetics of silicon & titanium minerals, the features of process itself and equipments in the current high-temperature-intensifying Bayer process are analyzed and compared. It is indicated that there are disadvantages in the current high-temperature-intensifying Bayer process for the complicated diaspore with difficulty to be digested. A new digesting process is proposed, i.e., tube preheating removal of silicon & titanium digestion in retention tank. This new process bears the advantages of the current digesting technology and better suitability for the complicated diaspore. It not only ensures better digesting results and lower energy consumption, but also reduces or eliminates the scales on the heat exchange surfaces, which makes the running period longer and investments smaller.

**3:40 PM Break**

**3:50 PM**
**Bayer Process Chemical Calculations ìA Systematic Approachî**: *Pradeep K. Maitra*[1]; [1]Balco, B-475 Cross St., 24 Smriti Nagar, Bhilai 490020 India

Till early 1990ís not much emphasis was given on productivity of Alumina. Subsequently because of stiff market competitions, the producers of alumina have to impose strict measures to optimise the specific consumption (SC) of raw materials e.g. bauxite, caustic soda, lime, etc. to reduce the cost of alumina production. In European bayer plant where huge quantity of caustic liquor recirculate continuously, it is extremely difficult to verify the process stock by physical method of stock taking, as a result the chemical stock often appeared to be in consistent with respect to its book values. To counter above discrepencies it was opined that the rate of consumption of raw material should be compared with the plant performances and the chemistry of the raw material, intermediate and finished product as well. In absence of National and International guidelines on chemical calculations of bayer process, the calculated values and expressions varies plant to plant. In above context an attempt has been made by the author to publish the simplified version of chemical calculations, so that in future time the same can be used for preparation of guidelines.

**4:20 PM**
**Influence of K2O in Spent Liquor on Bayer Process of Diasporic Bauxite**: *Zhonglin Yin*[1]; [1]Zhengzhou Research Institute, Aluminum Corporation of China, Ltd., Alumina Rsrch. Dept., Zhengzhou Light Metal Rsrch. Inst., Shangjie, Zhengzhou, Henan 450041 China

Illite, an impurity mineral existing in diasporic bauxite, causes K2O to accumulate in spent liquor and the concentration of K2O to increase gradually. The influence of K2O in spent liquor on the preheating process of slurry and digestion results is discussed in this paper. K2O in spent liquor can slow down the reaction rate of illite in preheating process of slurry and can reduce the Al2O3/SiO2 ratio Na2O/SiO2 ratio in red mud to a certain extent at some conditions. Therefore, the influence of K2O on the Bayer process must be considered in research studies of the Bayer process for diasporic bauxite.

**4:50 PM**
**Processing of Aluminium Ores and Human Safety**: Vadim A. Lipin[1]; Ludmila E. Safarova[1]; *Anatoly V. Sysoev*[2]; Alexander N. Aminov[2]; Valery P. Lankin[2]; [1]Russian National Aluminium-Magnesium Institute (VAMI), 86 Sredny pr., St. Petersburg 199106 Russia; [2]Bogoslovsky Aluminium Plant-JSC SUAL, 1 K. Marx str., Krasnoturinsk, Sverdlovsk Region 624440 Russia

The neutralization of industrial waste, including the alumina refineries was developed to create and improve the water sewerage and gas and dust scrubbing facilities at the final stages of process, less attention was paid to the establishing of waste free technology. The comprehensive way of alkaline alumo silicate ore practically excludes the solid and liquid wastes, typical for Bayer process as well as for conventional technology to produce the by-products. It can be achieved through the entire use of the products involved in the process, wide product range and diversity of thermal and hydro chemical areas.

**5:20 PM**
**New Salicylic Acid Containing Red Mud Flocculants**: *Everett C. Phillips*[1]; [1]Ondeo Nalco Company, Ondeo Nalco Ctr., Naperville, IL 60563-1198 USA

New, high molecular weight salicylic acid containing polymers have recently been developed at Ondeo Nalco Co. These new flocculants provide substantial improvements for the clarification of red mud decanter slurries from numerous Bayer plants, worldwide. The preparation and chemistry of these new polymers are summarized and compared to others used in the industry. Also presented are the developments to date, including mud settling, overflow clarity and liquor filtration results from both static and dynamic laboratory tests. The lab results demonstrate that the new salicylic acid containing flocculants can be applied without the need for starch, as is the case for traditional 100% polyacrylate polymers. A recent plant evaluation has confirmed this result.

## Aluminum Reduction Technology: Modeling

*Sponsored by:* Light Metals Division, LMD-Aluminum Committee
*Program Organizers:* Jay Bruggeman, Alcoa Inc., Alcoa Center, PA 15069 USA; Martin Segatz, VAW Aluminum Technology, Bonn D-53117 Germany; Paul Crepeau, General Motors Corporation, MC/486-710-251, Pontiac, MI 48340-2920 USA

Tuesday PM — Room: 6B
March 4, 2003 — Location: San Diego Convention Center

*Session Chair:* Don Ziegler, Alcoa Inc., Alcoa Tech. Ctr., Alcoa Ctr., PA 15069-0001 USA

**2:00 PM**
**An Analytical Model for Cathode Voltage Drop in Aluminum Reduction Cells**: *Richard M. Beeler*[1]; [1]Alcoa Inc., Hall Proc. Improv., 100 Technical Dr., Alcoa Ctr., PA 15069-0001 USA

This paper presents the derivation of an analytical model for cathode voltage drop (CVD) for typical cathode assemblies in aluminum reduction cells. The model includes an estimate of the current density profile on the cathode surface; the voltage profile along the length of the [current] collector bar; and a breakdown of total CVD into components between the carbon block, the collector bar, and the bar-block joint. Comparisons with a three dimensional finite element model are presented for evaluation of the severity of geometric simplifications. Model results, with joint resistance tuned to match typical plant CVDs, are presented to illustrate the distribution of total CVD between carbon blocks, collector bars, and bar-block joints.

**2:25 PM**
**START-Cuve: Thermo-Electro-Mechanical Transient Simulation Applied to Electrical Preheating of a Hall-HÈroult Cell**: *Martin DÈsilets*[1]; Mario Fafard[2]; Daniel Marceau[3]; [1]Alcan International Ltd., Arvida R&D Ctr., PO Box 1250, Jonquiere, Quebec G7S 4K8 Canada; [2]Laval University, Sci. & Eng. Fac., Adrien-Pouliot Bldg., Sainte-Foy, Quebec G1K 7P4 Canada; [3]University of Quebec at Chicoutimi, Appl. Sci. Dept., 555 Blvd. Universite, Chicoutimi, Quebec G7H 2B1 Canada

The phenomena taking place during the start-up of an aluminum reduction cell are complex and difficult to analyze. Experimental tests on industrial cells are difficult, time-consuming and expensive. Mathematical modeling offers here a good way to study the impact of design and start-up methods on thermo-mechanical equilibrium in a cell. An overview of the research program, called START-Cuve, involving industrial and university researchers, will be given. The material characterization part will be briefly described. The finite element modeling approach of the research program will then be developed more thoroughly. The numerical resolution of the fully coupled thermo-electro-mechanical problem, solved with a finite element code able to cope with complex constitutive laws, is a great challenge. In this paper, the architecture of the software is presented. The emphasis will be put on the multi-physic resolution in the context of simulating an electrical cell preheat, with a focus on three aspects: multi-field material constitutive laws, thermo-electro-mechanical contact between surfaces and numerical resolution of the problem. Finally, we present how finite element analysis can advantageously be combined with experimental test results to identify specific parameters using reverse engineering approaches.

**2:50 PM**
**Performing Fast Trend Analysis on Cell Key Design Parameters**: *Marc Dupuis*[1]; Warren Haupin[2]; [1]GeniSim, Inc., 3111 Alger St., Jonquiere, QC G7S 2M9 Canada; [2]Consultant, 2820 Seventh St. Rd., Lower Burrell, PA 15068-3717 USA

Four fast algebraic models that respectively calculate the anode panel heat loss, the cathode bottom heat loss, the anode voltage drop and the cathode voltage drop have been developed, compared with more complex ANSYSÆ based 3D thermo-electric finite element models and incorporated into the Dyna/Marc 1.7 lump parameters+ cell simulator. With the addition of those four algebraic models to the lump parameters+ cell simulator, it is now possible to perform fast trend analysis on key design parameters like the anode studs diameter, the stud holes depth, the collector bars size or the type of cathode blocks. In order to illustrate the increased power of the lump parameters+ cell simulator as a brainstorming session ìwhat ifî tool, the previously published retrofit study of a 300 kA cell into a 350 kA cell is repeated, this time using only the lump parameters+ cell simulator as modeling tool.

**3:15 PM**
**Modeling of the Coke Bed Used in the Electrical Preheat of an Aluminum Reduction Cell**: *Patrice Goulet*[1]; Carl Laberge[2]; RenÈ Lacroix[1]; Laszlo Kiss[2]; Jean Perron[3]; [1]Laval University, Sci. & Eng. Fac., Adrien-Pouliot Bldg., Sainte-Foy, QuÈbec G1K 7P4 Canada; [2]University of Quebec at Chicoutimi (UQAC), Appl. Sci. Dept., 555 Blvd. de líUniversitÈ, Chicoutimi, QuÈbec G7H 2B1 Canada; [3]Alcan International Ltd., Arvida R&D Ctr., PO Box 1250, JonquiËre, QuÈbec G7S 4K8 Canada

In the electrical preheat of aluminum reduction cell, deformations and stresses in all components of the cell are principally due to the temperature gradients. The temperature distribution is essentially established by the Joule effect in the electrical conductors. Furthermore, electrical current distribution is strongly dependent on the use of petroleum coke bed, playing the role of electrical resistor, placed between anode and cathode panels. The thermoelectric behavior of the bed is then an important factor on the preheat quality and must be included in a complete cell preheat model. The behavior of granular materials is usually represented by effective properties. However, it was observed experimentally that the contact quality between coke bed and a plane surface like anode blocks has an important effect on the electrical current and temperature distributions. In this respect, both thermal and electrical constitutive laws have to be developed. Constitutive laws parameters are calibrated by comparing experimental data with finite element model results using new contact elements.

**3:40 PM Break**

**3:50 PM**
**The Effect of Ambient Temperature and Ventilation on an Electrolysis Cellís Shell Temperature, Heat Balance and Ledge**: *Elin Haugland*[1]; *HÂvard B□rset*[1]; HÂvard Gikling[1]; Helge H□ie[2]; [1]Hydro Aluminium AS, Tech. Ctr. ≈rdal, PO Box 303, ÿvre ≈rdal 6884 Norway; [2]Hydro Aluminium AS, Karm□y Metal Plant, HÂvik 4265 Norway

The influence of ambient temperature and ventilation on an electrolysis cellís shell temperature, heat balance, and ledge thickness has been studied. Calculations have been carried out, using the commercial code FLUENT, to study the effect of variations in the ambient temperature on the shell temperature. The effect on the heat balance and the ledge has been calculated by means of Hydroís heat balance simulation model SMASH. Measurements have been carried out by placing thermocouples at the shell wall and in the ledge. A close correlation between the shell temperature and the ambient temperature has been found. No correlation has been found between ambient temperature and the total heat flux from the cell. Variations observed in heat flux can be traced to incidents at the cell; like anode changes, anode effects, changes in the reference resistance etc. The effect on the shell temperature, local heat flux and ledge thickness when the shell is cooled by means of air lances has also been studied. For a cell with ledge thickness 5-10 cm a relatively high decrease in shell temperature is needed before any changes in ledge thickness can be measured.

**4:15 PM**
**Minimization of Outward Wall Deformation of Cathode Casing Steel Structure During Operation**: *M. M. Megahed*[1]; H. S. Sayed[1]; Sh. A. Mohamed[1]; A. Abdel-Al[1]; F. M. Ahmed[1]; [1]Cairo University, Mechl. Design & Prod., Egyptalum, Nag-Hammadi Egypt

The paper describes the elaborate effort devoted at Egyptalum smelter toward minimizing the outward wall deformation during operation while keeping the weight of the cathode steel casing to a minimum. Starting from an existing pilot casing design, 16 design parameters are identified as the key controlling parameters affecting cathode structural behavior. Deformation and weight minimization is achieved through conducting consecutive systematic non-linear finite element structural analysis. A total of 17 consecutive design trials is investigated with each design trial stemming from its predecessor. The finite element analysis takes into account carbon swelling and its variation with time, plastic yielding and deformation of steel and its dependence on temperature. The finite element model is built using shell, beam and gap elements to represent the cathode steel structure and truss elements to represent the cathode carbon. Carbon swelling analysis is conducted using Dewing model with new parameters identified to reflect cathode technology employed at Egyptalum. The analysis is continued in real time up to a life of 1055 days of cell operation. Following each design trial, cathode weight, peak outward deformations of longitudinal and transverse walls were monitored and compared with earlier trial. On this basis, the key influencing structural parameters are identified and modified to reduce weight and deformations. The final cathode casing design exhibited almost the same weight as the original pilot design but with much less peak deformations. The results indicate that after three years of operation, the peak outward deformation of the longitudinal wall is about 60% of the corresponding value in the original pilot design. Similarly, the peak outward deformation of the transverse wall was about 34% of the corresponding value in the original pilot design.

**4:40 PM**

**Thermo-Chemo-Mechanical Aspects of Refractory Concrete Used in a Hall-HÈroult Cell**: *Daniel Richard*[1]; Mario Fafard[1]; Martin DÈsilets[2]; [1]Laval University, Sci. & Eng. Fac., Adrien-Pouliot Bldg., Ste-Foy, QuÈbec G1K 7P4 Canada; [2]Alcan International Ltd., Arvida R&D Ctr., PO Box 1250, JonquiËre, QuÈbec G7S 4K8 Canada

As part of the on-going project START-Cuve, involving the thermo-electro-mechanical modelling of a P-155 coke bed electrical preheating, the behaviour of the pier insulating refractory concrete had to be assessed. Preliminary experimental work has shown that even before preheating, large cracks were present in the concrete actually used for that technology. It was found that concrete hydration and drying caused shrinkage; also, the hydration reactions in calcium aluminate cement are extremely exothermic in nature, leading to substantial temperature gradients and free water vaporisation in the concrete while hardening. Therefore, the initial conditions in the pier concrete are rather inhomogeneous and complex to predict. As a first step, a macroscopic thermochemical constitutive law was used to represent the hydration reactions and their thermal effects. The hydration kinetics was reverse engineered by comparing experimental measurements in a quasi-adiabatic setup to a finite element model results. An experimental representative setup was then instrumented and modelled to validate the approach. A good agreement between the numerical and the experimental results was found.

**5:05 PM**

**On Some Features of Thermal State of HSS Cells**: *A. V. Sysoev*[1]; A. N. Aminov[1]; N. V. Markov[1]; G. S. Pryakhin[1]; T. V. Mezhberg[1]; [1]Bogoslovsky Aluminium Plant Russia

In 1997-2000 Bogoslovsky Aluminium Plant (Siberian-Ural Aluminium Company), equipped with HSS Soderberg cells, implemented an intensive technology in one potroom. The production rate increase amounted to 13.2%; in addition, specific consumptions of raw materials and power were reduced. Unusual technological features of the intensification were as follows: simultaneous increase of current density i‡ and current efficiency Ái; increase of Ái with increase of electrolyte overheating ƒT, electrolyte temperature decrease "e at increase of thermal losses in anode-to-cathode distance (ACD). Managerial and technological measures, providing the achievement of these performances, were based on optimization of the cell parameters and thermal balance. The investments were minimal, the repayment period was less than one year. The abnormality of the aforementioned features required thorough investigations on the peculiarities of distribution of heat sources and sinks in a cell by means of applied aspects of thermodynamics and electrochemical kinetics. Heat exchange mechanism is studied in ACD and at interface boundaries on the basis of the works by Polyakov P.V. and Mozhaev V.M., as well as Flem B.E. (L.M., 1996), Xu Q and Kjelstrup S (L.M., 1998). Under the cell normal state, when the Peltier heat at the anode completely compensates the heat of overvoltage of anode reaction (TƒS > ÁaI), the thermal flow from electrolyte to the anode is transferred mainly via anode side walls wetted with electrolyte. The areas of anode sole free from gaseous bubbles are characterized with very low transfer coefficient in comparison with the areas of anode walls and bubbled areas of anode sole. As the place of anode effect is approached (TƒS < ÁaI) a powerful heat source appears at the interface. Many abnormal features of anode effect occurrence can be explained by interference of physical phenomenon of intensive electrolyte evaporation into the electrochemical process. Analytical methods of the cell thermal state are developed on the basis of individual heat balances of ACD, anode and cell. The estimated value i‡ agrees with the actual one only in the case of application of the ACD heat balance and elimination of equilibrium voltage of decomposition (~1.19 V) from heating voltage. Comparative estimation of the features of heat losses from ACD of HSS, VSS Ë prebaked cells, highlighting the abnormal features of the intensive technology has been made.

## Carbon Technology - II

*Sponsored by:* Light Metals Division, LMD-Aluminum Committee
*Program Organizers:* Amir A. Mirchi, Alcan Inc., Arvida Research and Development Centre, Jonquiere, QC G7S 4K8 Canada; Don T. Walton, Alcoa Inc., Wenatchee Works, Malaga, WA 98828-9784 USA; Paul Crepeau, General Motors Corporation, MC/486-710-251, Pontiac, MI 48340-2920 USA

Tuesday PM — Room: 6D
March 4, 2003 — Location: San Diego Convention Center

*Session Chair:* Juan Romero, Alcan Inc., Alcan Primary Metal Grp, Robards, KY 42420 USA

**2:00 PM Cancelled**

**The Effect of Al-Containing Additives on Air/CO2 Reactivity of Carbon Anode in Aluminum Electrolysis**: *Yanqing Lai*[1]; Qingyu Li[1]; Jie Li[1]; Jianhong Yang[1]; *Yexiang Liu*[1]; [1]Central South University, Sch. of Metallurgl. Sci. & Eng., Changsha, Hunan 410083 China

**2:25 PM**

**Drilling of Stub Holes in Prebaked Anodes**: *Hogne Linga*[1]; [1]Hydro Aluminium, HAL Tech. Ctr. ≈rdal, PO Box 303, Ovre Ardal NO-6882 Norway

The stub holes may be a troublesome part in the production of anodes. Tension and cracks can be created around the stub hole. Vibrating the stub holes often introduce limitations for the optimisation of the production process. Stub holes oriented towards the cassette wall during baking will be filled with packing material. This requires the stub holes to be thoroughly cleaned after baking. Stub holes which are oriented away from the cassette walls, are unprotected during the baking process. This may lead to an increased rejection rate or additional costs to protect the stub holes. The paper will present four years of experience with drilling of the stub holes after the baking of the anodes. This technology allows for precision drilling of different designs of stud holes, and the paper will summarize the results from trials where three different designs are tested in the same reduction cell.

**2:50 PM Cancelled**

**Survey on Worldwide Prebaked Anode Quality**: *Raymond Perruchoud*[1]; Kirstine Hulse[2]; Markus Meier[1]; Werner Fischer[1]; [1]R&D Carbon, Ltd., Sierre 3960 Switzerland; [2]Alusaf Empageni S. Africa

**3:15 PM**

**The New AP-FCBA Paste Plant Technology**: *Christian Dreyer*[1]; *Corinne Jouault*[1]; AndrÈ Pinoncely[2]; Jean-FranÁois Andre[2]; [1]Aluminium Pechiney, LRF-BP 114, Saint Jean de Maurienne 73300 France; [2]FCB Aluminium, 32 Rue Fleury-Neuvesel, BP24-69702 Givors 69702 France

Aluminium Pechiney and FCB Aluminium jointly developed a new production process for the dry mix preparation. This new flow sheet reduces significantly both the investment and operating costs of a Paste Plant and allows for the production of an optimized G/S ratio. Based on promising preliminary Research & Development results and in order to fully validate such an innovative process, AP and FCBA invested in a full-scale trial program. The 35 tph industrial scale Pilot Plant which was built at the Aluminium Dunkerque smelter in Northern France has been successfully started in July 2002. This paper recalls the operating philosophy of that new plant and highlights the promising first technical results on anode quality obtained after the start up.

**3:40 PM Break**

**3:50 PM**

**Alcan Alma New Anode Paste Plant Start-Up and Early Operation**: *Claude Lavoie*[1]; Emmanuel Bergeron[1]; AndrÈ L. Proulx[2]; [1]Alcan Inc., Alcan Primary Metal Grp., Alma Works, 3000, Des Pins Ouest Ave., Alma, Quebec G8B 5W2 Canada; [2]Alcan Inc., Alcan Primary Metal Grp, 1955, Mellon Blvd., PO Box 1250, Jonquiere, Quebec G7S 4K8 Canada

Alcan announced in February 1998 the construction of an aluminium smelter in Alma, Quebec. The Alma smelter project was part of Alcanís corporate growth strategy and its Quebec smelter rebuilt program. For the anode paste plant, new principles and ideas originated from Alcan people experiences brought a new design. The new paste plant, an Alcan design, would be different compared to others in the aluminium industry. The Alma plant mixing line combines a discontinuous/continuous process based on three Eirich mixer/cooler units. The team preparation, the equipments commissioning and the start-up occurred in 2000-2001. The production ramp-up and the anodes quality were achieved in a short period of time despite necessary modifications. This paper will describe the Alcan Alma paste plant, its start-up and early operation.

**4:15 PM**

**New Plant for Anode Paste Conditioning and Anode Pressing with a Hydraulic Vacuum Press**: *Alfred Kaiser*[1]; [1]Laeis Bucher GmbH, Plant Eng., PO Box 8065, Trier D-54181 Germany

A new concept is presented for production of high quality anodes including innovative paste conditioning, dosing and mold filling system and a high performance hydraulic press with vacuum system. All components starting from outlet of the paste mixer are adjusted to provide a throughput of up to 60 large or 120 small anodes/h. Changes in paste properties are detected by the press control that immediately adjusts the paste conditioning/cooling mixer parameters. The precision of dosing system and press allows for an outstanding accuracy of anode height (?b 2 mm) with a very good reproducibility and an even density distribution within the anodes. The low pressing temperature of 115 to 130¢XC assures stable green blocks without water cooling and reduces emission of pitch volatiles (PAH etc.) Further advantages are low noise level (< 76 dBA), high flexibility and availability (e.g. mold change in less than 0.5 h) and low maintenance.

**4:40 PM**

**Paste Granulometry and Soderberg Anode Properties**: Morten Sorlie[1]; *Turid Vidvei*[1]; [1]Elkem Aluminium ANS Research, PO Box 8040, Vagsbygd, Kristiansand N-4675 Norway

There are almost as many different soderberg paste recipes as there are soderberg smelters, and most of them seem to perform satisfactory for the cells and cell operating parameters the pastes are made for. The baked anode properties may, however, be optimized by changes made to individual fractions and the total sieve curve. The paper discusses how green and baked soderberg anode properties change as the recipe particle distribution is changed, with special emphasis on the fineness of the fine fraction and the form of the total sieve curve.

**5:05 PM**

**The Technology Development of the Carbon Materials Industry for Aluminium Electrolysis in China**: *Fengqin Liu*[1]; [1]Zhengzhou Light Metal Research Institute, Dept. of Aluminum Electrolysis & Carbon, No. 82 Jiyuan Rd., Shangjie Dist., Zhengzhou, Henan Province 450041 China

The characteristics of raw material resources for the carbon material industry in China are discussed in this paper. The main production processes and equipment used to manufacture prebaked anodes, semi-graphitized cathodes, graphite cathodes and cathode paste in the industry are reviewed. The development trend and future of Chinese carbon material industry are pointed out in the paper as well.

## Cast Shop Technology: Filtration/Metal Treatment

*Sponsored by:* Light Metals Division, LMD-Aluminum Committee
*Program Organizers:* Jean-Pierre Martin, Aluminum Technologies Centre, c/o Industrial Materials Institute, Boucherville, QC J4B 6Y4 Canada; David H. DeYoung, Alcoa Inc., Alcoa Technical Center, Alcoa Center, PA 15069 USA; Seymour G. Epstein, The Aluminum Association, Inc., Washington, DC 20006 USA; Paul Crepeau, General Motors Corporation, MC/486-710-251, Pontiac, MI 48340-2920 USA

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| Tuesday PM | Room: 6C |
| March 4, 2003 | Location: San Diego Convention Center |

*Session Chairs:* Corleen Chesonis, Alcoa Inc., Alcoa Techl. Ctr., Alcoa Ctr., PA 15069 USA; Peter Waite, Alcan Inc., Arvida R&D Ctr., Jonquiere, QC G7S 4K8 Canada

**2:00 PM**

**Study of Al Degassing by Hydrogen Analysis with Supersonic Expansion Mass Spectrometry**: Marc Bertherat[2]; Elisabeth Blanquet[3]; *Michel Paul Allibert*[1]; Pierre Le Brun[4]; [1]Consultant, 23 Ave. Marcellin Berthelot, Grenoble 38100 France; [2]Aluminium Dunkerque, ZIP Ouest, BP81, Loon Plage 59279 France; [3]INPGrenoble, ENSEEG, BP75, St Martin díHeres 38402 France; [4]Pechiney Centre de Recherches de Voreppe, 725 rue Aristide Berges BP27, Voreppe 38341 France

The hydrogen extraction kinetics from liquid Aluminum by Argon degassing was studied using a mass spectrometer analyzing the out coming Argon, after supersonic expansion. This technique has a response time of less than 1 minute. Measurements were carried out on a 50 kg aluminum bath at 720∞C. Gassing of the metal was achieved by bubbling an Ar-5%H2 mixture for a long period. Argon was then distributed by one or several static nozzles. After a residence time of about 1 second the bubbles containing Ar and H2 were collected and a part of the resulting hot gas stream was expanded into a vacuum chamber where it was analyzed by a quadripole mass spectrometer. Hydrogen contents in this gas ranged from 0.1 to 2% with a measurement accuracy of about 0.1%. An on-line calibration by known Ar-H2 mixtures (1 to 10%) was used during the degassing period. Instantaneous variation of degassing parameters such as Ar flow rate, bubble size or stirring intensity were used to evidence the main features of the degassing macro-kinetics.

**2:25 PM**

**Critical Review of Published Values of Hydrogen Diffusion in Aluminum and its Alloys**: *Prince N. Anyalebechi*[1]; [1]Grand Valley State University, Padnos Sch. of Eng., L. V. Eberhard Ctr., Ste. 718, 301 W. Fulton, Grand Rapids, MI 49504-6495 USA

Published values of hydrogen diffusion in pure aluminum and its alloys have been critically assessed against three criteria, viz: (i) reliability of experimental techniques and methodologies, (ii) self-consistency of results reported by the same investigators, and (iii) agreement of reported results with theoretically predicted and well established empirical relationships. Empirical equations for calculating hydrogen diffusion in aluminum and its alloys derived from the most reliable published values are given. Reasons for the significant disparities between reported hydrogen diffusion values and for the paucity of reliable experimental data on hydrogen diffusion in commercial aluminum alloys (especially in the liquid and semi-solid states) are discussed.

**2:50 PM**

**Investigation of Inclusion Re-Entrainment During Filtration**: *Duygu Kocaefe*[1]; Audrey Murray-Chiasson[1]; Yasar S. Kocaefe[1]; Peter Waite[2]; [1]University of Quebec, Dept. of Appl. Scis., 555 Blvd. de líUniversitÈ, Chicoutimi, Quebec G7H 2B1 Canada; [2]Alcan International Ltd., PO Box 1250, Jonquiere, Quebec G7S 4K8 Canada

The fabrication of high quality aluminum products, requires filtration of the liquid alloy prior to casting. Inherent to deep bed filtration is not only inclusion separation from the metal (desired), but also a re-entrainment process whereby inclusions already deposited in the filter pores re-enter the liquid metal. Abrupt changes to the metal flow also cause inclusion re-entrainment negatively affecting metal quality. A better understanding of the fundamental mechanisms governing inclusion re-entrainment could be applied to improve industrial filtration processes. To investigate inclusion re-entrainment during deep bed filtration, an experimental water modeling study was carried out. It is a common practice to use water instead of aluminum due to similarities of key physical properties of the two liquids. PVC particles were used as inclusions. During experimentation, inlet and outlet inclusion concentrations are measured using LiMCA probes adapted for water. A kinetic expression defining inclusion deposition and re-entrainment is proposed taking into account the effects of inlet inclusion concentration, inlet liquid velocity and filter media particle size.

**3:15 PM**

**Aerospace Alloy Refining Efficiency Data for LARS (LARS: Liquid Aluminum Refining System)**: *Ravi Tilak*[1]; Jose Curiel[2]; [1]Almex USA, Inc., Cast House Sys., Long Beach, CA 90831 USA; [2]Vista Metals Company, QC, Fontana, CA 92335 USA

Since LARS metal treatment systems have been put into operation on aerospace alloys in 1997, several hundred million pounds of 2XXX and 7XXX alloys have been processed through LARS in conjunction with different downstream filtration media. This paper analyzes the quality of the finished product (i.e., plate, forgings and extrusions) as evaluated with various instruments and co relates it with the operating parameters of LARS. It is demonstrated that metal cast with in-line LARS and 50 PPI ceramic foam filtration is capable of consistently passing the Mil-2154-AA sonic inspection at the finished product stage. It is also demonstrated that by using LARS system, a plant can successfully eliminate the requirement of holding furnace in the typical cast-house set-up. (LARS is an acronym for Liquid Aluminum Refining System and is designed around three novel concepts; viz, in-situ preheating of inert process gas, attrition mixing of gas in liquid metal and prevention of bubble coalescence. LARS removes physical, chemical and metallurgical impurities from molten aluminum.

**3:40 PM Break**

**3:50 PM**
**Recent Experiences with the Use of SiO2 for Removing of Magnesium from Molten Aluminum Alloys**: *Alfredo Flores Valdes*[1]; Jose Escobedo Bocardo[1]; Jose Hernandez Gamez[1]; Sergio Escobedo Bocardo[2]; [1]CINVESTAV, Unidad Saltillo, PO Box 663, Saltillo, Coahuila 25000 Mexico; [2]Instituto Tecnologico de Saltillo, Blvd. V. Carranza y Ave. Universidad, Saltillo, Coahuila 25000 Mexico

The use of SiO2 for removing of magnesium from molten aluminum alloys has been studied in laboratory using submerged powders injection. The effects on the final magnesium and inclusions content of powder size, temperature of the molten alloy, and injection time were determined. The results obtained indicated the best experimental conditions to scaling up the process at cast shop level, for demagging of alloys containing of up to 3 wt. % Mg. In this paper it is reported both the results of the experiments conducted in laboratory, and the results of trials conducted in a cast shop facility. For the industrial trials, conducted in a reverberatory furnace, it was found that the use of fine grained SiO2 particles, and the powders injection at the point of higher turbulence, allowed to attain removal efficiencies above 60%. The presence of inclusions was not detected in the ingots obtained.

**4:15 PM**
**Computer Simulation of the Removal of Solid Particles from Molten Aluminum in the Rotating Impeller Degasser**: *Virendra Sitaram Warke*[1]; Makhlouf M. Makhlouf[1]; [1]Worcester Polytechnic Institute, Adv. Casting Rsrch. Ctr., Metal Processing Institute(MPI), 100 Institute Rd., Worcester, MA 01609 USA

One of the main tasks in aluminum refining is the removal of dissolved hydrogen and solid particles from the molten metal. This task is typically accomplished by means of a rotating impeller degasser. In this process, an inert gas, or a mixture of an inert and a reactive gas, is bubbled into the molten metal through a spinning nozzle. While the gas bubbles rise to the surface, they come in contact with suspended solid particles and dissolved hydrogen and carry them to the top slag. Currently, optimization of the rotating impeller degassing process relies to a large extent on operator experience; however, the demand for ever-increasing metal quality and cost effectiveness necessitates new approaches. Better understanding of the process can be achieved through computer modeling and simulations can be used to determine causes and corrective actions for specific operation problems. In this article, the rotary degassing melt treatment process is modeled using two interdependent modules. The first module simulates the flow field inside the furnace, and is based on two-phase fluid flow with free boundaries. The output from this module is the molten metal flow pattern, the gas bubble distribution, and the turbulence energy dissipation rate within the furnace. These parameters are used as input to the second module, which simulates the solid particles dynamics, including agglomeration, settling and flotation, as well as particle attachment to the gas bubbles and their subsequent rise to the sludge layer. The computer model is used to illustrate the effect of the various rotary degassing process parameters on process efficiency.

**4:40 PM**
**Physical Modeling of the Aluminum Degassing Process: Experimental and Mathematical Approaches**: *Emmanuel Waz*[1]; JÈrÙme CarrÈ[2]; Pierre Le Brun[1]; Alain Jardy[2]; Catherine Xuereb[3]; [1]PECHINEY CRV, 725, rue Aristide BergËs, BP 27, Voreppe, Cedex 38341 France; [2]LSG2M, Parc de Saurupt, Ecole des Mines de Nancy, Nancy, Cedex 54042 France; [3]LGC, UMR CNRS 5503 INP-ENSIACET, 5, rue Paulin Talabot, BP 1301, Toulouse, Cedex 1 31106 France

The paper proposes an experimental and numerical approach to analyze the removal of hydrogen from aluminum using rotor-based gas dispersion treatments. Liquid flows have been investigated experimentally in a water model (by Laser Doppler Velocimetry) in order to model molten aluminum flows in a degassing unit. A batch aluminum lab-scale treatment unit has been used to obtain data related to the kinetics of the degassing process. X-ray measurements have been used to assess relevant bubble characteristics (size and shape). These experiments have enabled to develop a numerical model of the aluminum degassing process, based on aluminum/argon two-phase flow. The model that accounts for the actual size and shape of the argon bubbles and the interfacial mass transfer phenomena allows the prediction of hydrogen removal kinetics in batch reactor, or hydrogen removal efficiency in in-line reactor, according to the experimental conditions.

**5:05 PM**
**Measurements of Bubble Dispersion and Other Bubble Parameters in a Gas Fluxing Unit at Alcoa Using a Capacitance Probe**: *James W. Evans*[1]; N. Mittal[1]; A. Fjeld[1]; D. Corleen Chesonis[2]; [1]University of California-Berkeley, Dept. of Matls. Sci. & Eng., Berkeley, CA 94720 USA; [2]Alcoa Inc., Casting Tech. Div., Alcoa Techl. Ctr., 100 Techl. Dr., Alcoa Ctr., PA 15069 USA

A capacitance probe has been developed at Berkeley that is intended to measure the frequency with which bubbles pass a point in liquid aluminum. The probe is comprised of an inner conducting wire (in some cases two wires) that is separated from the liquid aluminum by an alumina sheath. It works by detecting the change in capacitance, between the wire and the aluminum, which occurs when the aluminum moves back from the sheath as a bubble passes. Because only alumina is in contact with the melt, the probe is robust and can survive several hours in the metal. The software necessary for processing the signals from the probe is described. The probe has been used to measure bubbles in a fluxing unit at the Alcoa Technical Center and the difficulties in doing so are described. Results are presented and their relevance to modeling and optimization of fluxing units discussed. Research cofunded by DOE Energy Efficiency and Renewable Energy.

## Computational Methods in Materials Education: Market Perspectives and Teaching Materials

*Sponsored by:* TMS-Education Committee
*Program Organizers:* Zi-Kui Liu, Pennsylvania State University, Materials Science and Engineering, State College, PA 16082-5006 USA; Mark D. Asta, Northwestern University, Department of Materials Science and Engineering, Evanston, IL 60208-3108 USA; Long-Qing Chen, Pennsylvania State University, Materials Science and Engineering Department, University Park, PA 16802-5005 USA

Tuesday PM — Room: 13
March 4, 2003 — Location: San Diego Convention Center

*Session Chair:* Duane D. Johnson, University of Illinois Urbana-Champaign, Dept. of Matls. Sci & Eng. & Physics & the Frederick Seitz Matls. Rsrch. Lab., Urbana, IL 61801 USA

**2:00 PM Invited**
**A Perspective of Aerospace Structural Alloys and Computational Methods**: *Herbert A. Chin*[1]; John A. Miller[1]; [1]Pratt & Whitney, Matls. & Processes Eng., MS 114-42, 400 Main St., E. Hartford, CT 06108 USA

A perspective (past, present and future) of Structural Alloy in advanced gas turbine engines and opportunities for Computational Methods such as Thermo-Calc and DICTRA will be presented. Selected components from front to back of the engine will be discussed; goal requirements, challenges, and opportunities for Computational Methods to cost effectively bring those materials technologies to component insertion.

**2:30 PM Invited**
**Educational Needs for a New Materials Industry Based on Design**: *Charles J. Kuehmann*[1]; [1]QuesTek Innovations, LLC, 1820 Ridge Ave., Evanston, IL 60201 USA

A new revolution in computational materials design is changing what industry needs from new materials science graduates. This paradigm shift to design is being driven by new abilities to create the next generation of materials by computational design as well as the ever increasing cost of traditional empirical discovery. Currently, computational materials design expertise is limited to a small set of individuals, almost all with advanced degrees, many of whom have pioneered these enabling computational methods within their own graduate research. For the materials design revolution to take hold and grow, providing our profession a future, industry will need an available supply of young graduates with the computational and synthetic skills necessary to be effective contributors in the new companies and established organizations that embrace this coming revolution. Ad hoc attempts to provide computational content in curricula are not nearly as effective as approaches which integrate the theme into all aspects of teaching including basic thermodynamic and kinetic theory as well as applied course work specific to classes of materials, their processing, and ultimately their behavior. Ideally, these experiences should be reinforced by their integration via systems design within a capstone design course or project.

**3:00 PM Invited**
**The Enhancement of Materials-Oriented Textbooks by the Addition of Computer Software**: James W. Evans[2]; David R. Gaskell[3]; *Arthur E. Morris*[1]; [1]Thermart Software, 12102 Calle de Maria, San

Diego, CA 92128-2720 USA; [2]University of California, Matls. Sci. & Eng., 585 Evans Hall #1760, Berkeley, CA 94720-1760 USA; [3]Purdue University, Sch. of Matls. Eng., 1289 MSEE Bldg., W. Lafayette, IN 47907-1289 USA

Computational techniques are playing an increasing role in engineering education. One indicator is the number of engineering textbooks that contain CD-ROM disks with associated software. The content of several CD-ROM discs from materials textbooks is reviewed, and compared to CD content from chemical and mechanical engineering texts. The use of web pages to enhance the educational value of texts is also reviewed. Details are given of the CD disk material from new revisions of the following texts: ìProduction and Processing of Inorganic Materialsî, Second Edition, by James W. Evans and Lutgard C. De Jonghe (2002), and ìIntroduction to the Thermodynamics of Materialsî, Fourth Edition, by David R. Gaskell (2002). The CD for each text has two types of content. First, a large set of thermodynamic data as an Excel database, which extends the rather limited data often found in text appendices. Second, many examples (keyed to problems and exercises from the text) are solved using Excelís charting, data analysis, goal-seek and solver tools. Typical examples from each text are described.

**3:30 PM Break**

**4:00 PM Invited**
**Education in Computational Materials Science: Perspective from a National Laboratory**: *Andrew A. Quong*[1]; [1]Lawrence Livermore National Laboratory, Chem. & Matls. Sci., L-231, PO Box 808, Livermore, CA 94550 USA

At Lawrence Livermore National Laboratory, we have been involved in a number of activities that assist in the education of the Materials Science community. In particular, I will discuss two programs that I have been involved with over the past two years, the Lawrence Livermore National Laboratory Computational Materials Science and Chemistry Summer Institute for graduate students and a tutorial at the Materials Research Society meetings in Computational Materials Science. The goal of the Institute is to provide an opportunity for graduate students to explore cutting-edge methods in computational materials sciences, computational chemistry, and other related areas of computational science during their first few years of graduate study. Each student spends eight weeks at LLNL as the guest of an LLNL host scientist working on a computational project in the hostís area of expertise. The purpose of the tutorial at the MRS was to introduce the many facets of multi-length scale modeling. Because of the growing interest in the field of multiple length scale modeling, this tutorial provided the attendees with a balanced description of the main facets of this field as applied in materials science. The tutorial consisted of lectures and a hands-on computer session where the attendees were able to run actual applications.

**4:30 PM Invited**
**Recommended Skill Sets for Future Engineers in the Aluminum Industry**: *Hasso Weiland*[1]; [1]Alcoa Technical Center, 100 Techl. Dr., Alcoa Ctr., PA 15069 USA

Development times for new products in the materials industry have shortened significantly. While earlier, the development of a new alloy took several decades, now two to three years are the standard. To achieve such short development times, it is required to have well integrated materials simulation tools available. Such tools are to be based on accurate understanding of the underlying processes. These changing needs in the materials industry requires engineers and scientists to have sound knowledge in several disciplines. This presentation attempts to outline the skill sets necessary for successful future candidates.

**5:00 PM Panel Discussion**

## Computational Phase Transformations: Effect of Interface on Phase Transformation

*Sponsored by:* ASM International: Materials Science Critical Technology Sector, Electronic, Magnetic & Photonic Materials Division, Structural Materials Division, Materials Processing & Manufacturing Division, ASM/MSCTS-Thermodynamics & Phase Equilibria Committee, MPMD-Computational Materials Science & Engineering-(Jt. ASM-MSCTS), Jt. EMPMD/SMD-Chemistry & Physics of Materials Committee, Phase Transformation Committee-(Jt. ASM-MSCTS)
*Program Organizers:* Yunzhi Wang, The Ohio State University, Department of Materials Science and Engineering, Columbus, OH 43210 USA; Perry Leo, University of Minnesota, Department of Aerospace Engineering and Mechanics, Minneapolis, MN 55455 USA; Ralph E. Napolitano, Iowa State University, Ames Laboratory, Department of Materials Science and Engineering, Ames, IA 50011 USA; Vidvuds Ozolins, Sandia National Laboratories, Livermore, CA 94551-0969 USA; Wolfgang Windl, The Ohio State University, Department of Materials Science and Engineering, Columbus, OH 43210 USA

Tuesday PM Room: 11B
March 4, 2003 Location: San Diego Convention Center

*Session Chairs:* Long-Qing Chen, Pennsylvania State University, Dept. of Matls. Sci. & Eng., University Park, PA 16802 USA; J. E. Morral, University of Connecticut, Dept. of Metall. & Matls. Eng., Storrs, CT 06269-3136 USA

**2:00 PM Invited**
**Impurity-Induced Grain Boundary Phase Transformations in Metals and Oxides**: *Gerd Duscher*[1]; [1]North Carolina State University, Dept. of Matls. Sci. & Eng., Solid State Div., 2156 Burlington Nuclear Lab., Raleigh, NC 27695-7916 USA

It has been suspected for a long time that impurities can induce grain boundary phase transformations. It is difficult, however, to prove this transformation, since to do so we must study unexpected atomic arrangements at the core of grain boundaries. This can only be accomplished by using a combination of experimental and theoretical studies at atomic resolution. In this study, we used Z-contrast imaging, electron energy-loss spectroscopy (EELS) and ab initio materials simulations to study the atomic structure of grain boundaries. Z-contrast imaging provides us with directly interpretable images of the grain boundary structure, and EELS characterizes the chemical composition locally at the core of the grain boundary. The resolution of both of these techniques is greatly enhanced with an aberration corrector, which allows subangstrom analysis. The first results obtained with an aberration-corrected STEM are shown in this study. These experimental results allowed us to produce a starting model for ab initio calculations. We used ultrasoft pseudopotential and a plane wave basis set method in local density approximation. The total energies for the models with and without impurities allowed us to find the lowest energy configuration. While the grain boundary structure changed dramatically with Ca impurities in MgO, we saw only a slight modification in sigma 5 Al grain boundaries with Cu doping. However, there is no grain boundary phase transition of Cu grain boundaries with heavy dopant atoms (Bi, Ag).

**2:30 PM Invited**
**Beyond the Local-Equilibrium Paradigm in Phase Transformation Modeling**: *John A.L. ≈gren*[1]; [1]Royal Institute of Technology, Dept. of Matls. Sci. & Eng., Stockholm 100 44 Sweden

Finite interfacial mobility and solute diffusion across interfaces may cause a deviation from local equilibrium during phase transformations and cause, for example, a transition to massive transformation at some critical supersaturation. Exactly where this transition occurs depends on the kinetics of the interfacial reactions. Another question concerns the transition to paraequilibrium during the transformation of austenite in steels. Even though these phenomena have been discussed for almost half a century the progress has been very slow until the last few years. Many papers have been published recently. There are several reasons for this, e.g. the new development of bainitic steels has awakened the old paraequilibrium concept, the recent phase-field theory includes (unknown?) details of phase interfaces and new experimental techniques allows to characterize the chemical constitution of interfaces with a higher precision. In this presentation some recent advances in the modeling of the above phenomena will be discussed.

**3:00 PM**
**Effect of Grain Boundaries on Spinodal Decomposition**: *Hariharaputran Ramanarayan*[1]; Thennathur A. Abinandanan[1]; [1]Indian Institute of Science, Dept. of Metall., Bangalore, Karnataka 560 012 India

We have used a combination of a phase field model (a continuum version of the Potts model) and the Cahn-Hilliard model to study the effect of grain boundaries (g.b.) present in a polycrystalline sample on spinodal decomposion. In particular, when $\gamma_\alpha < \gamma_\beta$ (i.e., when the grain boundary (GB) energy of the A-rich α phase is less than that of the B-rich β phase), the early stage is characterized by a preferential migration of A atoms to the GB. This process leads to a composition wave that travels normal to the GB into the grain interior, and to the formation of alternating B-rich and A-rich bands near the GB. Simultaneously, grain interiors, unaffected by the GB, undergo normal SD. Thus, the late stage microstructures in large grains reveal alternating bands of α and β phases near GBís coexisting with normal SD microstructure in the grain interiors. On the other hand, small grains (whose sizes are 2 to four times the characteristic spinodal wavelength), exhibit only concentric, alternating rings of the α and β phases. In this paper, we will present these results with an emphasis on the factors that affect the extent of the banded regions near the GB relative to the normal SD region in the interiors.

**3:20 PM Break**

**3:40 PM Invited**
**Some Recent Comparisons Between Experiment and Modeling of Interfaces in Phase Transformations**: *James M. Howe*[1]; William C. Johnson[1]; [1]University of Virginia, Dept. of Matls. Sci. & Eng., 116 Engineerís Way, Charlottesville, VA 22904-4745 USA

This presentation discusses two recent examples where experiments and modeling were combined to better understand the role of interfaces in phase transformations in solids. In one example, a two-dimensional Cahn-Hilliard equation was used to model the experimentally observed spinodal decomposition in the presence of a solute-depleted zone adjacent to Ag-rich plates in an Al-Ag alloy. In the second example, variational calculus was used to model the experimentally observed dependence of the dihedral angles at a triple junction on the fraction of Ag and Cu-rich phases in spherical two-phase, Ag-Cu alloy particles. In both cases, the modeling was found to reproduce the experimentally observed behavior, thereby leading to a better understanding of the fundamental phenomena causing the behavior as well as enabling new behaviors to be explored. This research was supported by NSF under Grants DMR-9902110 and 9908855.

**4:10 PM Invited**
**Phase Field Modeling of Polycrystals**: *James A. Warren*[1]; [1]NIST, CTCMS, 100 Bureau Dr., Stop 8554, Gaithersburg, MD 20899 USA

A two dimensional phase field model of grain boundary statics and dynamics has been developed. The model, which introduces an orientation parameter to the well known phase field model of solidification, reproduces many of the phenomena observed during grain boundary evolution, as well as the phenomenon of grain rotation. The theory also predicts the onset of grain boundary wetting, above a critical grain misorientation where the grain boundary energy exceeds twice the liquid-solid surface energy. In this talk we examine some of the new areas of application of this model, including alloys, fractal structures, spherulitic growth and some of the mathematical idiosyncrasies of the model (in particular, how to deal with the non-analytic free energy density). Finally, we will discuss future avenues for research.

**4:40 PM**
**Integrity of Grain Boundaries in an Al-Li-Cu-Mg-Zr Alloy: Experimental Observations and Modelling Opportunities**: *Graham B. Winkelman*[1]; Stan P. Lynch[2]; Barry C. Muddle[1]; [1]Monash University, Sch. of Physics & Matls. Eng., PO Box 69M, Victoria 3800 Australia; [2]Defence Science and Technology Organisation, PO Box 4331, Melbourne, Victoria 3001 Australia

A limiting factor in the up-take of Li-containing Al alloys for commercial applications remains the susceptibility of the alloys to low energy intergranular fracture at low temperatures. In the present work, the susceptibility to embrittlement of an Al-Li-Cu-Mg-Zr alloy (commercial alloy 8090) has been associated with the segregation of Li to grain boundaries during ageing. The fracture behaviour of the material thus sensitised is observed to be strongly temperature-dependent, with the sensitised alloy undergoing a sharply-defined transition from ductile to brittle intergranular fracture with decreasing temperature. Preliminary evidence suggests that this transition may be associated with a two-dimensional structure change within the Li-modified grain boundaries as a function of temperature. The experimental approaches to this problem will be summarised, along with consideration of the needs for computational modelling to assist in elucidating details of both the structural transitions within the grain boundaries and the subsequent fracture behaviour.

**5:00 PM**
**Thermal Transient FEA of Lead Anode Casting Mould**: *Zane Jia*[1]; Reg Davis[1]; Jenny Cassidy[1]; Gary Morin[2]; [1]H. G. Engineering, 400 Carlingview Dr., Toronto, Ontario M9W 5X9 Canada; [2]Falconbridge, Ltd., Kidd Creek Div., PP Box 2002, Timmins, Ontario P4N 7K1 Canada

A thermal transient finite element analysis (FEA) study was performed to help solve problems associated with the poor lead anode quality of the lead anode casting mould. The study was intended to evaluate the transient heat transfer between the lead anode and the casting mould. A 3D FEA model of lead anode casting mould, including multi-phase lead anode was created. Non-linear transient thermal analyses were performed to evaluate the lead anode solidification process. FEA results of the current casting process match the field observation and measurements closely. Therefore the FEA model now provides the client a unique tool in quantifying the current casting process, and consequently identifying the problems. A preliminary modification design was performed to improve the mould cooling to produce better quality lead anodes. The proposed modifications were further evaluated through the modified FEA models. Results of the FEA clearly demonstrate the benefits of the proposed modifications.

## Defects and Deformation of Crystalline Solids - in Honor of Dr. Man H. Yoo - IV

*Sponsored by:* ASM International: Materials Science Critical Technology Sector, Electronic, Magnetic & Photonic Materials Division, Structural Materials Division, Jt. EMPMD/SMD-Chemistry & Physics of Materials Committee, SMD-Mechanical Behavior of Materials-(Jt. ASM-MSCTS), SMD-Physical Metallurgy Committee
*Program Organizers:* Jong K. Lee, Michigan Technological University, Metallurgical & Materials Engineering Department, Houghton, MI 49931-1200 USA; Sean R. Agnew, University of Virginia, Materials Science and Engineering Department, Charlottesville, VA 22904-4745 USA; K. N. Subramanian, Michigan State University, Department of Material Science & Mechanics, East Lansing, MI 48824-1226 USA

Tuesday PM　　Room: 17A
March 4, 2003　　Location: San Diego Convention Center

*Session Chairs:* Armen Khachaturyan, Rutgers University, Dept. of Matls. Sci. & Eng., Piscataway, NJ 08855 USA; Tresa Pollock, University of Michigan, Matls. Sci. & Eng. Dept., Ann Arbor, MI 48109-2136 USA

**2:00 PM Invited**
**Relationship Between Deformation and Recrystallization Textures**: *Dong Nyung Lee*[1]; [1]Seoul National University, Sch. of Matls. Sci. & Eng., Seoul 151-744 Korea

The recrystallization process basically occurs to reduce the energy stored during fabrication. The stored energy may include energies due to vacancies, dislocations, grain boundaries, surface, etc. The energy is not directional, but the texture is directional. No matter how high the energy of defects may be, they cannot directly be related to the recrystallization texture, unless they give rise to some anisotropic characteristics. The most important driving force for recrystallization is known to be the stored energy due to dislocations. Dislocations cannot be related to the recrystallization texture, unless they give rise to some anisotropic characteristics. In this article, we discuss how dislocations generated during deformation can give rise to anisotropic characteristics for recrystallization textures.

**2:25 PM Invited**
**Deformation Mechanisms of Slip Transmission in Alpha/Beta Titanium Alloys at Lower Temperatures**: *Michael J. Mills*[1]; [1]The Ohio State University, Matls. Sci. & Eng., 478 Watts Hall, Columbus, OH 43210 USA

Two-phase titanium alloys such as Ti-6242 and Ti-6Al-4V are used extensively in aeroengine and biomedical applications. In spite of their high strength, Ti alloys must be employed conservatively because of their tendency to creep significantly at room temperature, even at stresses well below the macroscopic yield strength. The transmission of slip across α-β interfaces, which conform to a near-Burgers orientation relationship, is an important precess during creep. Testing of single colony crystals of both Ti-5Al-2.5Sn and Ti-6242 has shown that they are highly anisotropic with respect to the operative slip system in the α-phase. Extensive TEM investigation has revealed the mechanisms of slip transmission for various orientations, which provides insight into the observed anisotropy in yield and creep behavior. The implications of these results with respect to modeling of deformation and fatigue in Ti alloys will also be discussed. Funding for this work has been provided by the US Air Force Office of Scientific Research and the Federal Aviation Administration.

**2:50 PM**

**Displacement Mapping of Intermetallics at the Length Scale of Individual Grains**: *Gurjeev Chadha*[2]; Aomin Wu[2]; Qidi Chen[1]; Marc De Graef[1]; Tresa M. Pollock[2]; [1]Carnegie Mellon University, Matls. Sci. & Eng., 5000 Forbes Ave., Pittsburgh, PA 15213-3890 USA; [2]University of Michigan, Dept. of Matls. Sci. & Eng., H. H. Dow Bldg., 2300 Hayward St., Ann Arbor, MI 48109-2136 USA

In many intermetallics, local microstructural variations affect plastic deformation. Such variations include texture (differently oriented grains react differently to a given load), segregation, multiple phases, etc. We have developed a two-dimensional displacement mapping technique to determine in-plane surface displacements during mechanical testing (tension and compression). The method requires the deposition of a square grid of markers on the sample surface. Images are taken at different load levels, and a semi-automated pattern recognition system determines the displacements of the markers with respect to reference marker positions. Strain levels of less than 0.1% can thus be measured, with multiple measurements for each individual grain (grain size 10-100 micron). A combination of displacement mapping and orientation imaging microscopy can provide sufficient information to analyse strain levels in terms of the available slip systems for each individual grain. We will present strain maps for a variety of materials, including RuAl, IN100, and Mg.

**3:10 PM**

**Microcracking in Brittle Materials Due to Thermal Expansion Anisotropy**: *Phani Kumar Nukala*[1]; Srdan Simunovic[1]; Balasubramaniam Radhakrishnan[1]; Gorti B. Sarma[1]; [1]Oak Ridge National Laboratory, Compu. Sci. & Math. Div., Oak Ridge, TN 37831-6359 USA

Thermal cooling of a variety of polycrystalline materials from high processing temperatures results in microcracking due to thermal expansion anisotropy of single phases and/or thermal expansion mismatch between multiple phases. This study investigates the damage evolution in polycrystalline materials due to thermally induced microcracking using three-dimensional discrete lattice spring networks. In particular, the effect of grain size distribution on inter- and intragranular microcrack nucleation, growth and coalescence is investigated. Realistic 3D microstructure based discrete lattice simulations include the interaction of grains in parallel planes and the additional crack propagation paths for growth and coalescence of cracks. Numerical simulations are also used to estimate the critical grain size below which nucleation of microcracks does not occur. This critical grain size plays an important role in designing material applications with improved fracture properties. This work also highlights the significant differences between 2D and 3D numerical simulation of thermally induced microcracking in polycrystalline materials. Work performed under the auspices of the US Department of Energy by Oak Ridge National Laboratory under Contract DE-AC05-00OR22725 with UT-Batelle LLC.

**3:30 PM Break**

**3:50 PM Invited**

**Mechanical Properties of Single Crystals of $Mo_5SiB_2$ and Related Compounds**: Kazuhiro Ito[1]; *Masaharu Yamaguchi*[1]; [1]Kyoto University, Dept. of Matls. Sci. & Eng., Sakyo-ku, Kyoto 606-8501 Japan

$Mo_5SiB_2$ is a new refractory metal silicide with great potential for ultra-high temperature structural applications. We have grown high purity single crystals of $Mo_5SiB_2$ and related compounds by an optical floating zone method. Single-crystal electric resistivity, thermal expansion coefficient (CTE) and elastic constants of these compounds were measured in a wide temperature range. Compression and creep tests at high temperatures were also performed. The results of these experiments are presented all together.

**4:15 PM**

**Phase Field Microelasticity Theory and Modeling of Elastic Inhomogeneities, Voids and Cracks**: *Yu U. Wang*[1]; Yongmei M. Jin[1]; Armen G. Khachaturyan[1]; [1]Rutgers University, Ceram. & Matls. Eng., 607 Taylor Rd., Piscataway, NJ 08854 USA

Technologically advanced solid materials are frequently inhomogeneous, both elastically and structurally. The effect of elastic inhomogeneities on material properties is less understood than that of structural inhomogeneities due to its more complicated theoretical treatment. The Phase Field Microelasticity approach is employed to formulate a general theory of different modulus solid, which provides an effective tool to model arbitrary elastic and structural inhomogeneities. Voids and cracks are the particular cases of this theory. They are treated as inhomogeneities of zero elastic modulus. This approach reduces the problem of elastic equilibrium and evolution of an inhomogeneous system to a solution of the non-linear integro-differential Ginzburg-Landau equation. In the Phase Field formalism, the long-range strain-induced interaction of individual inhomogeneities is directly taken into account. The proposed model does not impose a priori constraint on possible inhomogeneity configurations or their evolution paths. Examples of effect of elastic inhomogeneities on material microstructures and properties are presented.

**4:35 PM Invited**

**Microstructural Stability in Non-Equilibrium Processed Alloys**: Yong C. Kim[1]; Sang B. Lee[1]; Seung J. Hwang[2]; Kwang S. Shin[3]; *Nack J. Kim*[1]; [1]POSTECH, Ctr. for Adv. Aeros. Matls., San 31, Hyojadong, Pohang 790-784 Korea; [2]Daejin University, Dept. of Matls. Sci. & Eng., Kyung-gi 487-711 S. Korea; [3]Seoul National University, Seoul 151-742 S. Korea

In recent years, there has been a renewed interest in non-equilibrium processes such as mechanical milling/alloying and rapid solidification, since these can produce powders with a nanoscale grain size and a homogeneous distribution of nanoscale dispersoids. However, it is known that the nanoscale microstructures of non-equilibrium processed powders are lost during high temperature consolidation, often resulting in undesirable microstructures. Although most of the non-equilibrium processed alloys still show much finer grain size after consolidation than conventionally processed alloys, it is needed to restrict grain growth as much as possible to maximize the potential of non-equilibrium processed alloys. The present study is aimed at investigating the evolution of microstructure in non-equilibrium processed alloys during subsequent consolidation. Various types of alloys have been investigated in the present study, including Al-, Mg-, Ni-, and Ti-based alloys. Emphasis has been placed on the role of dispersoid particles in microstructural stability of these alloys.

**5:00 PM**

**The Role of Polytwin Interfaces for the Deformation Behavior of L1o-Ordered Iron-Palladium Intermetallics**: *J˜rg M.K. Wiezorek*[1]; [1]University of Pittsburgh, Matls. Sci. & Eng., 848 Benedum Hall, Pittsburgh, PA 15261 USA

The frequent polytwin (PT) interfaces present in L1o-phases after appropriate heat treatments strongly influence the properties and behavior of this interesting class of intermetallics. The interactions of dislocation glide and mechanical twinning with the PT-interfaces has been studied through crystallographic and geometric analyses for {101}-conjugated PT-interfaces in FePd based L1o-phases. PT-FePd alloys exhibit a yield stress anomaly and considerable work-hardening under tensile conditions. Defect-interface interactions in room temperature deformed PT-FePd have been studied experimentally by transmission electron microscopy (TEM). A model for the defect-interface interactions in PT-FePd, based on the most suitable boundary reactions, identified through theoretical analyses, has been proposed and is consistent with the experimental TEM observations. This model enables a micro-mechanism based rationalization of the plastic flow behavior typical of polycrystalline PT-FePd. Defect-interface interactions in {101}-conjugated PT-L1o-phases and their role for the deformation behavior of are discussed. This work has been supported by the NSF, grant DMR 0094213, with Dr. K.L. Murty as program manager.

## Dynamic Deformation: Constitutive Modeling, Grain Size, and Other Effects: Symposium in Honor of Professor Ronald W. Armstrong: Dynamic Fracture

*Sponsored by:* Structural Materials Division, ASM International: Materials Science Critical Technology Sector, SMD-Mechanical Behavior of Materials-(Jt. ASM-MSCTS)
*Program Organizers:* Marc Andre Meyers, University of California-San Diego, Department of Mechanical and Aerospace Engineering, La Jolla, CA 92093-0411 USA; George T. Gray III, Los Alamos National Laboratory, Dynamic Properties Team, Los Alamos, NM 87545-0001 USA; Naresh Thadhani, Georgia Institute of Technology, School of Materials Science and Engineering, Atlanta, GA 30332-0245 USA; Kenneth S. Vecchio, UC San Diego, Dept of Mechanical and Aerospace Engineering, La Jolla, CA 92093-0411 USA

Tuesday PM        Room: 16B
March 4, 2003     Location: San Diego Convention Center

*Session Chair:* Kenneth S. Vecchio, University of California-San Diego, Mechl. & Aeros. Eng., La Jolla, CA 92093-0411 USA

**2:00 PM**
**Role of Disperson Forces in Fracture**: *John J. Gilman*[1]; [1]University of California-Los Angeles, Matls. Sci. & Eng., 6532 Boelter Hall, Los Angeles, CA 90095-1595 USA

Dispersion forces between atoms are small and therefore usually ignored. However, they are always positive, and when integrated over many atoms in a dense solid, they become significant over short distances. In particular, near the tips of cracks. As the local chemical bonding forces become weak due to tensile strains, the dispersion forces become important. The former forces increase proportionally with strain for small strains (Hookeís Law), whereas the latter forces decrease in proportion to large strains cubed (Lifshitz Law). A single functional dependence describes the combined forces from zero to large strains in terms of the elastic stiffness and the polarizability (no disposable parameters). High polarizability extends the size of the region of plastic deformation; and the roughness caused by plastic deformation increases the dispersion forces. Thus the nature of ductility can be understood.

**2:30 PM**
**The Structure and Distribution of Voids in Spall Fracture from 3D X-Ray Tomography and 2D Microscopy**: *James Belak*[1]; James Cazamias[1]; David Haupt[1]; John Kinney[1]; Mukul Kumar[1]; Roger Minich[1]; Robert Rudd[1]; Chris Schuh[1]; Adam Schwartz[1]; Eira Seppala[1]; [1]Lawrence Livermore National Laboratory, PO Box 808, Livermore, CA 94550 USA

Gas gun recovery experiments were used to study incipient spall fracture in polycrystalline aluminum and single crystal aluminum and copper. In addition to in-situ VISAR waveprofiles, the recovered samples were first analyzed using 3D X-ray tomography and then sectioned for 2D microscopy. Void nucleation and growth in the polycrystal samples occurs at grain boundaries with an exponential distribution of void sizes. The void size and spatial distribution are determined directly from the X-ray tomography. The single crystal samples show a bimodal distribution of small voids with large (50-100 micron) well separated voids. The plastically damaged region surrounding the large voids is quantified using optical and electron backscattering microscopy. Microhardness measurements indicate this region to be harder than the surrounding metal. This work was performed under the auspices of the US Department of Energy by University of California, Lawrence Livermore National Laboratory under Contract W-7405-Eng-48.

**2:45 PM**
**Laser-Based Experiments Investigating the Dynamics of Ductile Material Failure**: *Kimberly S. Budil*[1]; Daniel H. Kalantar[1]; Richard C. Becker[1]; Geoffrey H. Campbell[1]; F. Xabier Garaizar[1]; James F. Belak[1]; Daniel J. Nikkel[1]; [1]Lawrence Livermore National Laboratory, DNT/B Div., PO Box 808, L-97, 7000 East Ave., L-97, Livermore, CA 94550 USA

We will describe an effort to develop a laser-based testbed to study dynamic material failure. Laser drivers produce extremely high strain rates (10^6-10^8 /sec) and can be used to produce shocked or shockless, quasi-isentropic compressions. A main focus is the development of in situ diagnostics including probing the pressure history within the sample (via free surface velocity measurements), observing the formation and evolution of voids (via x-ray radiography) and measuring the response of the lattice to compression (via dynamic diffraction). We are developing an experiment to measure the growth rate of an isolated void in a material that has gone into tension after shock passage and will present calculations and preliminary data for the proposed experiment. This work was performed under the auspices of the US Department of Energy by University of California, Lawrence Livermore National Laboratory under Contract W-7405-Eng-48.

**3:00 PM**
**Spall Behavior of Laser-Shocked Sn: Comparison of Modeling to Experimental Data**: *Jeffrey D. Colvin*[1]; E. R. Ault[1]; T. L. Clauson[1]; W. E. King[1]; M. Kumar[1]; I. H. Zimmerman[1]; [1]University of California, Lawrence Livermore Natl. Lab., L-356, PO Box 808, Livermore, CA 94550 USA

Few-joule table-top lasers can generate pressures up to the 100-kbar range in materials by propagating a low-intensity beam through a transparent dielectric, which confines the ablation pressure, onto an ablation layer in contact with the material of interest. We have applied this technique to the study of spall in Sn and other metals. Application of this technique to material deformation studies has been hampered until recently by lack of a physically based model of the laser absorption processes. We describe a new computational model for these processes incorporated into a 2D radiation-hydrodynamics code. We discuss this model through a comparison of simulated and measured free-surface velocity histories for Sn, and review the implications for spall models. This work was performed under the auspices of the US DOE by the Univ. of Calif., LLNL under Contract No. W-7405-Eng-48.

**3:15 PM**
**Spall Studies in Single and Polycrystalline Copper**: *James U. Cazamias*[1]; Adam J. Schwartz[2]; Roger L. Minich[3]; Mukul Kumar[4]; [1]Lawrence Livermore National Laboratory, L414, PO 808, Livermore, CA 94551 USA; [2]Lawrence Livermore National Laboratory, L-355, PO 808, Livermore, CA 94551 USA; [3]Lawrence Livermore National Laboratory, L-097, PO 808, Livermore, CA 94551 USA; [4]Lawrence Livermore National Laboratory, L-356, PO 808, Livermore, CA 94551 USA

We are executing a systematic study to quantify the effects of specific microstructural features on the spall behavior of 99.999% copper. Spall in ductile metals is a 1D strain dynamic tensile failure caused by the nucleation, growth, and coalescence of voids. Previous work reported an increase in spall strength of polycrystalline copper with increasing grain size. Here, we will present results of single crystals with [100], [110] and [111] orientations, and internally oxidized [100] single crystals (0.15 and 0.5 wt.% Si) that are shocked with Cu flyers at velocities ranging from 300 to 2000 m/s using a 35-mm single/two-stage light gas gun. The presence of hard silica particles in the microstructure provide potent nucleation sites for void nucleation and reduce the spall strength dramatically in comparison to the pristine single crystals. Laser interferometric measurements of the free surface velocity are used to characterize the spall pullback signal and details of the ringing. This work was performed under the auspices of the US Department of Energy by the University of California, Lawrence Livermore National Laboratory under contract No. W-7405-Eng-48.

**3:30 PM**
**Stress-Strain Description of Elastic, Plastic, Cracking Behavior of Microstructurally Biased Two-Phase TiB2+Al2O3 Ceramic**: *Louis Ferranti*[1]; Naresh N. Thadhani[1]; [1]Georgia Institute of Technology, Sch. of Matls. Sci. & Eng., 771 Ferst Dr., Atlanta, GA 30332 USA

Vickers microindentation hardness testing was used to investigate the elastic, plastic, and cracking behaviors of microstructurally biased two-phase TiB2+Al2O3 ceramic. An indentation hardness stress-strain description considering the classical analysis of Hertz was constructed to evaluate the theoretical elastic behavior for the total indentation event. Comparison of the presumed entirely plastic hardness measurement with the elastic Hertzian hardness stress-strain description indicated a significant elastic contribution to the measurement. Individual Hertz elastic stress-strain curves were constructed for pure TiB2 and Al2O3 as well as the two-phase TiB2+Al2O3 ceramic determined by the rule of mixtures. These curves were accompanied by experimentally measured hardness values on four quantitatively unique microstructures. This analysis enables the comparison of hardness measurements with those predicted by the Hertz description and the contributing elastic effect during the measurement processes. The analysis also illustrates the need for precise nanometric scale measurements to determine this elastic effect directly from experimental material testing methods. Continuous ball indentation hardness testing from previous studies dramatically shows the importance of the elastic component for the predicted hardness values (Armstrong 1995, Hammond 1988).

**3:45 PM Break**

**4:00 PM**

**Morphology of Fracture Domains in Brittle Solids**: *Michael Grinfeld*[1]; T. W. Wright[1]; [1]Educational Testing Service and National Research Council, 9 Carlton Cir., Princeton, NJ 08540 USA

The appearance of intensively fractured zones (IFZ) is a rather widespread phenomenon when dealing with brittle materials in various engineering systems or with geophysical media. Since even individual defects of a crystalline medium like cracks, dislocations, interfaces, etc. are complex objects on their own, researchers limit themselves with an overall, integral description of the IFZís material. When dealing with IFZ it is often desirable to extend the information about the overall material properties with the information about the overall shape and morphology of the IFZ. In this paper, following Gibbs and Griffith minimum energy approaches, we propose one such thermodynamic approach allowing one to determine the shape of the IFZ simultaneously with the distributions of stresses and strains within the systems of interest. The general methods and results of the suggested approach are illustrated by consideration of some particular brittle systems taken from engineering and geomechanics.

**4:15 PM**

**A Model for Fracture of Explosively Driven Metal Shells**: *Vladimir M. Gold*[1]; Ernest L. Baker[1]; [1]US Army TACOM-ARDEC, Attn: AMSTA-AR-WEE-C, Bldg. 3022, Picatinny Arsenal, NJ 07806-5000 USA

A model for fracture of explosively driven metal shells presented in this work is based on integrating three-dimensional axisymmetric hydrocode analyses with analyses from a newly developed fragmentation computer code MOTT. The developed model was based on the Mottís theory of break-up of cylindrical ìring-bombsî, in which the length of the average fragment is a function of the radius and velocity of the shell at the moment of break-up, and the mechanical properties of the metal. The validation of the MOTT code fragmentation model was accomplished using the existing explosive fragmentation munition arena test data. After having established the crucial parameters of the model, a new explosive fragmentation munition was designed and optimized. Upon fabrication of the developed munition, the performance of the new charge was tested in a series of small-scale experiments including the flash radiography, the high-speed photography, and the sawdust fragment recovery. The accuracy of the MOTT code predictions is rather remarkable.

**4:30 PM**

**Failure Behavior of Tungsten-Reinforced Amorphous Metal Matrix Composites**: *L. J. Kecskes*[1]; L. S. Magness[1]; T. Jiao[2]; T. C. Hufnagel[2]; K. T. Ramesh[2]; [1]US Army Research Laboratory, Weapons & Matls. Rsrch. Direct., Aberdeen Proving Ground, MD 21005 USA; [2]The Johns Hopkins University, Baltimore, MD 21218 USA

We evaluated the ballistic behavior of tungsten-reinforced bulk-metallic glass (BMG) matrix composites. Special techniques were employed to recover the residual penetrators and penetrator erosion products. To delineate the ballistic behavior from those observed at lower strain rates, we conducted a series of compressive split-Hopkinson-pressure-bar (SHPB) tests at strain rates of about 103 s-1. The failure surfaces of monolithic and composite samples obtained in the high-strain-rate tests as well as those of the ballistic erosion products were examined with scanning electron microscopy (SEM). X-ray diffraction (XRD) analysis of the ballistic debris and SHPB sample fragments revealed little or no crystallization. These results are consistent with the primary failure mechanism of the BMG matrix being governed by a drop in viscosity due to a temperature increase associated with shear localization.

**4:45 PM**

**The Dependence of Spall Strength on Length Scales**: *Roger W. Minich*[1]; Mukul Kumar[1]; James Cazamias[1]; Adam J. Schwartz[1]; [1]Lawrence Livermore National Laboratory, 7000 East Ave., Livermore, CA 94550 USA

The spall process involves nucleation, growth and coalescence of voids leading to final fracture. It is now widely accepted that the microstructure exerts a strong influence on the resistance of a material to spallation. Data in the literature indicates that the spall strength of high purity Cu single crystals is about twice that of polycrystalline Cu. This clearly indicates the influence of intercrystalline defects such as grain boundaries and triple junctions. Systematic variation in pressure suggests that the spall strength increases with increasing grain size, peaking for the single crystal case. This functional dependence of the flow stress on microstructural length scales is being developed into a model for implementation into 1-D finite element formulations. The model incorporates statistical stress fluctuations due to microstructural effects that increase the probability that a void can nucleate and grow thereby decreasing the spall strength, as for example, as a function of grain size.

**5:00 PM**

**AFM Studies of Fracture Surfaces of Composition B Energetic Materials**: *Yvonne D. Lanzerotti*[1]; Jagadish Sharma[2]; R. W. Armstrong[3]; [1]US Army TACOM-ARDEC, AMSTA-AR-WEE, Bldg. 3022, Picatinny Arsenal, NJ 07806-5000 USA; [2]Naval Surface Warfare Center, Carderock Div., W. Bethesda, MD 20817-5700 USA; [3]AFRL-MNME, 2306 Perimeter Rd., Eglin AFB, FL 34542-5910 USA

The characteristics of TNT (trinitrotoluene) crystals in Composition B have been studied using atomic force microscopy (AFM). The size of TNT crystals has been examined by analyzing the surface structure that is exhibited after mechanical failure of the Composition B. The mechanical failure occurs when the material is subjected to high acceleration (high g) in an ultracentrifuge and the shear or tensile strength is exceeded. AFM examination of the topography of the Composition B fracture surface reveals fracture across columnar grains of the TNT. The width of the columnar TNT grains ranges in size from 1 micron to 2 microns. Their height ranges in size from 50 nanometers to 300 nanometers.

**5:15 PM**

**Effect of Triaxiality on Void Growth in Dynamic Fracture: A Molecular Dynamics Study**: *Eira T. Sepp%d%o*[1]; James Belak[1]; Robert E. Rudd[1]; [1]Lawrence Livermore National Laboratory, L-415, 7000 East Ave., Livermore, CA 94550 USA

Dynamic fracture in ductile metals occurs through the nucleation and growth of voids. In this paper the effect of stress triaxiality on the evolution of the void growth has been studied in a single-crystal copper under dilational strain. Molecular dynamics simulations have been performed with a pre-existing void using high strain rates ranging from 10^7/sec to 10^10/sec and uniaxial, biaxial, and triaxial loading modes. Stress-strain curves, void shape evolution, and dislocation structures for the different loading modes are analyzed showing that the yield stress, the growth-rate and isotropicity of the void, and the dislocation activity are dependent on the triaxiality. Acknowledgment: This work was performed under the auspices of the US Dept. of Energy at the University of California/Lawrence Livermore National Laboratory under contract no. W-7405-Eng-48.

**5:30 PM**

**Void Initiation and Growth in Spalling**: *Vlado A. Lubarda*[1]; Bimal K. Kad[1]; Matthew S. Schneider[1]; Fabienne Gregori[2]; Marc A. Meyers[1]; Daniel H. Kalantar[3]; Bruce A. Remington[3]; [1]University of California-San Diego, Mechl. & Aeros. Eng., 9500 Gilman Dr., La Jolla, CA 92093-0411 USA; [2]University of Paris, 13 Villetaneuse, Paris 93430 France; [3]Lawrence Livermore National Laboratory, Livermore, CA 94720 USA

The various existing mechanisms for void initiation and growth are discussed in terms of their applicability to the high-strain rate regime. The relative importance of diffusional processes (vacancies) and slip processes (dislocations) are discussed in the establishment of void initiation and growth relationships. The mechanisms are compared with observations in plate impact and laser shock experiments. Research supported by the Department of Energy.

## Friction Stir Welding and Processing II: Friction Stir Joining: Corrosion & Corrosion Fatigue

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

*Program Organizers:* Kumar V. Jata, Air Force Research Laboratory, Materials & Manufacturing Directorate, WPAFB, OH 45433 USA; Murray W. Mahoney, Rockwell Science Center, Thousand Oaks, CA 91360 USA; Thomas J. Lienert, University of South Carolina, Mechanical Engineering Department, Columbia, SC 29208 USA; Rajiv S. Mishra, University of Missouri-Rolla, Metallurgical Engineering, Rolla, MO 65409-0340 USA

Tuesday PM Room: 7B
March 4, 2003 Location: San Diego Convention Center

*Session Chair:* Murray W. Mahoney, Rockwell Science Center, Thousand Oaks, CA 91360 USA

**2:00 PM**
**Corrosion and Stress Corrosion Susceptibility of Friction Stir Welded in Al-Li-Cu Alloy AF/C458**: *Rudolph G. Buchheit*[1]; Barbara N. Padgett[1]; Christian S. Paglia[1]; [1]Ohio State University, Dept. of Matls. Sci. & Eng., 477 Watts Hall, 2041 College Rd., Columbus, OH 43210 USA

Among Al-Li-Cu alloys, AF/C458 (Al-1.8Li-2.7Cu-0.6Mg-0.3Zn) exhibits good localized corrosion and stress corrosion cracking (SCC) resistance in aqueous chloride solutions. However, susceptibility to both is increased near of friction stir welds due to microstructural changes induced by the thermal excursion associated with welding. Intergranular corrosion has been detected in the weld nugget, thermomechanically affected zone (TMAZ), and in the heat affected zones (HAZ). Under dynamic straining in chloride solutions with loads applied transverse to the weld, SCC occurs in the HAZ near the interface with the TMAZ. In this location, deformation is concentrated due to local softening during welding. At this interface, grain boundaries become oriented perpendicular to the load direction. These boundaries are rendered electrochemically active due to heavy precipitation of $T_1$ ($Al_2CuLi$) on them. Special consideration will be give to the possibility that boundaries containing the $T_B$ ($Al_7Cu_4Li$) are less susceptible to attack than those where $T_1$ has precipitated.

**2:25 PM**
**Localized Corrosion and Stress Corrosion Cracking of Friction Stir Welds in 7XXX Aluminum Alloys**: *Rudolph G. Buchheit*[1]; Christian S. Paglia[1]; Anthony P. Reynolds[2]; [1]Ohio State University, Fontana Corrosion Ctr., 477 Watts Hall, 2041 College Rd., Columbus, OH 43210 USA; [2]University of South Carolina, Dept. of Mechl. Eng., Columbia, SC 29208 USA

Localized corrosion and stress corrosion cracking (SCC) behavior of friction stir welds in 7075-T6 and 7150-T7 is presented. In the as-welded condition, localized corrosion susceptibility is increased in the heat affected zones (HAZ) of the weld. Localized corrosion occurs as intergranular corrosion and pitting at constituent particles in the alloy. TEM and local electrochemical measurements suggest that precipitation at grain boundaries leads to intergranular corrosion. SCC failures also occur in HAZs. SCC was characterized by constant extension rate tests of samples cut transverse to the weld. SCC susceptibility results in decreased yield stresses and ductility. Deformation is concentrated in soft HAZs sections occurs in heat affected zones due. Local softening and increased grain boundary precipitation appear to be the primary contributing factors. Several post weld heat treatment processes are described with particular attention paid to short term high temperature treatments that result in uniform weld hardness and good SCC resistance.

**2:50 PM**
**Improving Corrosion Properties of 7475 Friction Stir Welds by Localized Heat Treatment**: Ali A. Merati[2]; Don Raizenne[2]; *Claudio Dalle Donne*[1]; [1]German Aerospace Center, Inst. of Matls. Rsrch., Linder Hoehe, Cologne 51147 Germany; [2]National Research Council Canada, Inst. for Aeros. Rsrch., 1500 Montreal Rd., Bldg. M-13, Ottawa, Ontario K1A 0R6 Canada

Recent work in the field of 7xxx aluminum alloy friction stir welds revealed that joints of these materials have to be heat treated after welding to stabilize the weld microstructure and to increase the stress corrosion properties. Even though only specific areas of the weld and heat affected zone require post-weld heat treatment, the entire welded plate is normally aged in an oven. From a production point of view this procedure is cost and labor intensive. This paper deals with the retrogression and re-aging (RRA) heat treatment carried out locally on double and single pass welds of 10 mm thick 7475-T7351. The RRA heat treatment was specifically developed for 7075 alloys in an attempt to achieve high levels of both strength and stress corrosion cracking (SCC) resistance. The hardness and conductivity measurements of the locally heat treated welds are compared to the values of plates treated in an oven. Moreover the results of tensile and stress corrosion (ASTM G139) tests are presented.

**3:15 PM**
**High-Cycle Corrosion Fatigue of 7050-T7451**: *Michael Dunlavy*[1]; Kumar V. Jata[1]; [1]Air Force Research Laboratory, Matls. & Mfg. Direct., AFRL/MLLM, 2230 Tenth St., WPAFB, OH 45503 USA

Due to their heterogeneous microstructures and susceptibility to pitting corrosion extensive research has been performed on the effects of friction stir welding (FSW) on corrosion fatigue behavior of 2xxx and 7xxx series high strength aluminum alloys. However limited work has been done on high-cycle corrosion fatigue behavior of high strength FSW aluminum alloys, such as 7050-T7451. The objective of this work was to evaluate the effect of pitting corrosion on high cycle fatigue strengths of friction stir welded aluminum alloy 7050-T7451 after exposure to prohesion spray. Various exposure times (100 and 500 hrs) during prohesion tests resulted in corrosion pits, which were measured after fatigue testing. HCF tests were conducted near the endurance limit and fracture surface analysis determined whether failure originated at corrosion pits or inclusion sites.

**3:40 PM Break**

**3:50 PM**
**Effects Pre and Post Weld Heat Treatments on the Corrosion Properties and Microstructure of FSW Zones of AA7075 and AA7050**: *Jesse B. Lumsden*[1]; Cecil Rhodes[1]; Murray Mahoney[1]; [1]Rockwell Scientific, 1049 Camino Dos Rios, Thousand Oaks, CA 91360 USA

The corrosion properties of high strength aluminum alloys is strongly dependent on grain boundary composition as well as the composition and morphology of the intermetallics. Thus, the corrosion behavior of the recrystallized microstructure in the nugget of a FSW aluminum alloys is usually different from that of the parent material. In addition the local temperature occurring during FSW is sufficiently high to cause dissolution, nucleation, and/or coarsening of the strengthening intermetallics in the weld heat affected zone (HAZ) and the thermo-mechanically affected zone (TMAZ). Our investigations have shown that transformations in the TMAZ/nugget interface of AA7050-T7 and the HAZ of AA7075-T6 and -T7 produce a sensitized microstructure, increasing susceptibility to intergranular attack, pitting and stress corrosion cracking (SCC). Measurements of the pitting potential and the SCC susceptibility, using the slow strain rate technique, have identified pre and post weld heat treatments which restore the corrosion resistance of the weld zones in these alloys. Changes in the corrosion properties of these materials will be compared with changes in the composition and morphology of the precipitates.

**4:15 PM**
**Microstructure and Stress Corrosion Cracking Behavior of Friction Stir Welded Al Alloys**: *Efstathios I. Meletis*[1]; [1]Louisiana State University, Mechl. Eng. Dept., Nicholson Ext., Baton Rouge, LA 70803 USA

Friction stir welding (FSW) was utilized to join a series of high-strength Al alloys, namely AA 2195, AA 2219 and AA 7075. All alloys were in the form of 0.23" thick plate, in the peak-aged temper. The microstructures of the various FSW zones were characterized by transmission electron microscopy. The stress corrosion cracking (SCC) behavior of the welded alloys was studied by conducting two types of experiments. First, four-point bending experiments were carried out in 3.5% NaCl solution under alternate immersion for 90 days. Second, slow extension rate tests (SERT) were conducted in laboratory air after different pre-exposure periods in NaCl solution under alternate immersion. Selective open circuit potential measurements of the various FSW zones were also conducted. The SCC behavior of the FSW alloys is discussed in view of the present experimental findings and current understanding of SCC behavior of Al alloys.

**4:40 PM**
**Corrosion Fatigue Crack Growth and Initiation in FSW and GMA Welded Al 2519**: *Peter S. Pao*[1]; E. Lee[2]; C. R. Feng[1]; H. N. Jones[1]; [1]Naval Research Laboratory, Code 6323, Washington, DC 20375 USA; [2]Naval Air Warfare Center, Aircraft Div., Patuxent River, MD 20670 USA

The corrosion-fatigue crack propagation and initiation characteristics of friction stir welded (FSW) and gas metal arc (GMA) welded Al 2519 in air and in salt water were investigated. TEM studies reveal the presence of very fine θí in the base metal, the coarsening of θí and the formation of //021 in the FSW HAZ, and the dissolution of most of the θí in the FSW weld. Microhardness mapping was obtained for both FSW and GMA welds to illustrate the drop in hardness in both weld and HAZ. Fatigue crack growth rates in the FSW weld and HAZ are significantly lower the threshold is significantly higher than those in the base metal. These changes may be attributed to the compressive residual stresses at the crack tip. Fatigue crack initiation lives of FSW welds are longer than GMA welds and the fatigue threshold of FSW weld approaches that of the base metal and is significantly higher than GMA weld.

**5:05 PM**
**The Joint Properties of Dissimilar Formed A356 and 6061 Al Alloys by Friction Stir Welding Method**: *Won Bae Lee*[1]; *Seung Boo Jung*[1]; *Yun-Mo Yeon*[2]; [1]SungKyunKwan University, Adv. Matls. Eng., 300 ChanAn-Gu, ChunChun-Dong, Suwon, Kyonggi-Do 440-746 Korea; [2]Suwon Science College, Automatic Welding Eng., Jungnam-myun, Botong-ri, Whasung, Kyoggi-do Korea

We observed the mechanical and metallurgical properties of friction stir welded joints of casting A356 Al alloy and wrought 6061 Al alloy whether these specimens fixed at retreating or advancing side. The specimens which was fixed at the retreating side mainly dominated the microstructure of stir zone. In case the 6061 Al alloys was fixed at the retreating side, the microstructure of stir zone was composed of mainly recrystallized structure of 6061 Alloys and some A356 Al alloy. The hardness of weld zone was slightly increased compare to that of A356 base metal due to the dispersed Si particles on Al matrix, but it showed lower hardness than that of 6061 Al alloys because the precipitates existed in base metal were dissolved at the weld by welding heat. In case of longitudinal tensile test, 6061 Al alloys which was fixed at the retreating side showed higher value than opposite case.

## General Abstracts: Steels and Non-Metals

*Sponsored by:* TMS
*Program Organizers:* TMS, Warrendale, PA 15086 USA; Eric M. Taleff, University of Texas, Mechanical Engineering Department, Austin, TX 78712-1063 USA

Tuesday PM — Room: 19
March 4, 2003 — Location: San Diego Convention Center

*Session Chair:* Eric M. Taleff, University of Texas, Mechl. Eng. Dept., Austin, TX 78712-1063 USA

**2:00 PM**
**The Effects of Carbon Content on the Tempering Response of R-Phase Strengthened Martensitic Stainless Steels**: *Aytekin Hitit*[1]; Warren M. Garrison[1]; [1]Carnegie Mellon University, Dept. of Matls. Sci. & Eng., 5000 Forbes Ave., Pittsburgh, PA 15213 USA

We have investigated the effect of nickel contents varying from 4.5 to 6 wt.% on the strength and toughness if a 0.005C/12Cr/12Co/5Mo base steel. It was found that nickel additions enhanced strengthening by particles of R-phase and also improved the room-temperature Charpy impact energy. Nickel contents of 6 wt.% were associated with much lower ductile-to-brittle transition temperatures than those of the alloys containing smaller amounts of nickel. In this work the effects of carbon contents of 0.005, 0.25 and 0.05 wt.% on the properties of 12Cr/12Co/5Mo/4.5Ni and 12Cr/12Co/5Mo/4.5Ni alloys were investigated. For a nickel level of 4.5 wt.% increasing the carbon content increased the peak strength after tempering and lowered the temperature at which the peak strength was observed from 550∞C to 525∞C. Also, at a nickel content of 4.5 wt.% increasing the carbon content from 0.005 to 0.25 wt.% increased the peak hardness by 3 Rc and increasing the carbon level from 0.025 to 0.05 wt.% resulted in no further increase in hardness. At the nickel content of 6 wt.% increasing the carbon content increased the peak strength after tempering but did not change the temperature at which the peak strength was observed, 525∞C. In general it would appear that small additions to alloys of this type can result in substantial increases in strength without substantially reducing the room temperature impact energy.

**2:20 PM**
**The Effects of Combining R-Phase and NiAl Strengthening on the Strength and Toughness of Martensitic Precipitation Strengthened Stainless Steel**: *Aytekin Hitit*[1]; Warren M. Garrison[1]; [1]Carnegie Mellon University, Dept. of Matls. Sci. & Eng., 5000 Forbes Ave., Pittsburgh, PA 15213 USA

We have investigated the effect of nickel contents varying from 4.5 to 6 wt.% on the strength and toughness if a 0.005C/12Cr/12Co/5Mo base steel. It was found that nickel additions enhanced strengthening by particles of R-phase and also improved the room-temperature Charpy impact energy. Nickel contents of 6 wt.% were associated with much lower ductile-to-brittle transition temperatures than those of the alloys containing smaller amounts of nickel. While the toughness characteristics of the 6 wt.% nickel alloy were excellent the strength of the alloy was not sufficient for the alloy to be considered for landing gear applications. The purpose of this work was to investigate whether or not NiAl strengthening due to the introduction of aluminum would result in strength and toughness levels necessary for an alloy of this type to be considered for use in landing gear applications. For this work aluminum additions of 0.5, 0.72 and 0.9 wt.% were made to a 0.005/12Cr/12Co/5Mo/6Ni base steel. The required strength levels could only be achieved at an aluminum content of 0.9 wt.% but the toughness at this strength level was low.

**2:40 PM**
**Crystallographic Influences on Bainite Kinetics and Morphology in Fe-C-Mo**: *R. E. Hackenberg*[1]; G. J. Shiflet[2]; [1]Los Alamos National Laboratory, Matls. Sci. & Tech. Div. (MST-6), MS G770, Los Alamos, NM 87545 USA; [2]University of Virginia, Dept. of Matls. Sci. & Eng., Charlottesville, VA 22904-4745 USA

Diffusive processes often limit the growth of pearlite and bainite in alloy steels; crystallographic effects are thought to play only a minor role. Recent work on Fe-0.24C-4Mo decomposed at its bay temperature will be presented which highlights the significant influence of crystallography on the austenite decomposition microstructures. Observations of a significant substructure of differently oriented ferrite subunits (containing alloy carbides) in grain boundary-nucleated bainite are instrumental for understanding the faster thickening kinetics of grain boundary bainite relative to twin boundary bainite. This substructure originates in the crystallography of nucleation at grain and twin boundaries, and has significant consequences for the growth behavior. An additional finding, the observation of stepped ferrite + fibrous carbide growth fronts, calls into question the prior understanding that such growth fronts are incoherent.

**3:00 PM**
**Investigation of Bainite Formation Using Neutron Bragg-Edge Transmission**: *Jin Huang*[1]; Sven Vogel[2]; Mark Bourke[2]; Warren J. Poole[1]; Vincent Yuan[2]; Pascal Jacques[3]; [1]University of British Columbia, Dept. of Metals & Matls. Eng., #309-6350 Stores Rd., Vancouver, BC V6T 1Z4 Canada; [2]Los Alamos National Laboratory, Struct. Prop. Relations (MST-8), Matls. Sci. & Tech. Div., MS H805, Los Alamos, NM 87545 USA; [3]University catholique de Loivain, Faculte des Scis. Appliquees, Dept. des Scis. des Materiaux, UCL-PCIM, 2 Place Sainte Barbe, Louvain-La-Neuve B-1348 Belgium

Structural phase transformations in solids can be investigated in-situ and in real-time using the Bragg-edge transmission technique. Neutron Bragg-edge transmission provides the crystallographic parameters volume fraction, lattice parameter and reflection width of participating phases with temporal resolutions in the order of tens of seconds. Additionally to the good temporal resolution, the neutron transmission setup allows to rapidly change sample temperature of bulk samples relatively homogeneously by splitting the sample into several disks. We demonstrate the technique by applying it to the investigation of the austenite decomposition to bainite in a silicon-rich steel. From the volume fraction, lattice parameter and edge width information we are able to derive information on transformation kinetics, carbon concentration and carbon homogeneity in the two phases, respectively. The findings of the neutron transmission measurements are compared with independent materials characterization methods like dilatometry, X-ray diffraction and metallography.

**3:20 PM**
**Characterization of the Nucleation and Growth Behavior of Copper Precipitates in a Low Carbon Steel**: *Michael S. Gagliano*[1]; Morris E. Fine[2]; [1]Ondeo Nalco, Dept. of Metall., One Ondeo Nalco Ctr., Naperville, IL 60563 USA; [2]Northwestern University, Dept. of Matls. Sci. & Eng., 2225 N. Campus Dr., Evanston, IL 60208 USA

The nucleation and growth behavior of copper precipitates in ferrite were investigated both theoretically and experimentally in low carbon steel with and without niobium additions. Theoretical nucleation and growth rate models were constructed using calculated thermodynamic data in conjunction with classical theories. The maximum nucleation and growth rates for Cu were determined to be about 1016 nuclei/cm3s at 612C and 0.038 nm/s at 682C. Using an experimentally determined ìeffectiveî activation energy for the diffusion of copper, the theoretical nucleation rate curve compared very well with the hardness data after only 5 minutes of aging. The growth and coarsening behavior of the Cu precipitates were investigated through conventional TEM for isothermally aged samples cooled directly to the aging temperature immediately following austenitization. For aging times up to five hours, the average precipitate size scaled with a time dependence of while longer aging times showed a time dependence of t0.28.

**3:40 PM Break**

**3:50 PM**
**Structured Methodologies for Material Processing Solutions**: *ReneÈ Miller*[1]; [1]John Deere, Heat Treat, PO Box 270 D188, Waterloo, IA 50704-0270 USA

Data Focus, Decision Analysis, Juran QIP and Design of Experiments are a few of the quality and management tools available to assist Metallurgists in resolving material processing issues. This paper will briefly outline the concepts of these tools, their advantages, and examples of their applications in material processing.

**4:10 PM**
**Quantification of Structural Disorder in Oxide Glasses: Quantum Chemical Calculations and Spectroscopic Analysis**: *Sung Keun Lee*[1]; [1]Carnegie Institution of Washington, Geophysl. Lab., 5251 Broad Branch Rd., Washington, DC 20015 USA

Oxide glasses, including borosilicates and aluminosilicates and their precursor liquids, have long been studied because of their diverse applications in the glass and ceramic industry and the strong implications of their structures to the properties of magmas. Essential to the macroscopic thermodynamic and transport properties of oxide glasses and melts is the full understanding of the atomic arrangements and the extent of disorder among atoms. However, quantitative estimation of the extent of the inherent disorder in silicate glasses and melts has remained a complex and difficult problem, largely because of the limits of resolution of conventional experimental techniques. Here, we present our recent results on quantification of the disorder and site connectivity among framework cations and oxygens in alumino- and borosilicate glasses using multi nuclear multiple quantum (MQ) magic angle spinning (MAS) NMR and quantum chemical calculations based on density functional theory (DFT). These methods combined with statistical mechanical modeling allowed us to evaluate the extent of disorder in terms of the degree of Al-avoidance and degree of phase separation and provided improved understanding of the configurational thermodynamic properties of corresponding melts. Several oxygen sites (e.g. Si-O-Al, Al-O-Al, B-O-B, B-O-Si, and Si-O-Si) are clearly resolved in O-17 MQMAS NMR spectra of alumino- and borosilicate glasses. About 10% Al-O-Al in NaAlSiO4 glasses suggests that Al-avoidance is imperfect in fully polymerized aluminosilicate glasses and melts. The degree of Al avoidance (Q) in Ca- and Na- aluminosilicate glasses from the experimental data ranges from 0.95-0.85 where Q=1 and 0 refers complete Al avoidance and random distribution respectively. From the DFT calculated relative energy differences among each oxygen cluster in binary borosilicate glasses (Si-O-Si, Si-O-B, and B-O-B), the stability of Si-O-B was quantified. The fraction of Si-O-B at XB=0.57 is about 36.5 % (±1), suggesting a significant inter-dispersion of B and Si, while a random distribution of Si and B and clustering of similar framework lead to 50 and 0% of Si-O-B respectively. This prediction is consistent with experimental results from O-17 3QMAS NMR. The similar methods have been extended to the study of the extent of disorder in mixed cation glasses where several types of non-bridging oxygen such as Na-O-Si, Ca-O-Si, Ba-O-Si and (Ca,Na)-O-Si are well resolved under O-17 MQMAS NMR. The oxygen site population data as well as Na-23 NMR results supports the random distribution of each cation. We also calculated configurational thermodynamic properties including configurational heat capacity and entropy as a function of composition, temperature and as well as the extent of Al avoidance and phase separation, which shows remarkable similarity with experimental results by solution calorimetry.

**4:30 PM**
**Evaluation of Ionic Liquids as Heat Transfer Fluids for Solar Thermal Parabolic Trough Technology**: Ramana G. Reddy[1]; *Mario F. Arenas*[1]; Zhijing Zhang[1]; [1]The University of Alabama, Metallurgl. & Matls. Eng., PO Box 870202, Tuscaloosa, AL 35487 USA

Long-term thermal stability and corrosivity against engineering materials are important for the evaluation of ionic liquids as potential energy storage and heat transfer fluids for solar thermal power systems. In this investigation, thermogravimetric analyses (TGA) and electrochemical corrosion tests were carried out on various ionic liquids, namely 1-butyl-3-methylimidazolium chloride ([$C_4$mim]Cl), 1-hexyl-3-methylimidazolium hexafluorophosphate ([$C_6$mim]$PF_6$), 1-octyl-3-methylimidazolium hexafluorophosphate ([$C_8$mim]$PF_6$), and 1-butyl-3-methylimidazolium bis(trifluromethanesulflonyl)imide ([$C_4$mim][$Tf_2$N]). Experimental results showed that these ionic liquids exhibit a highest decomposition temperature of 400∞C. However, long-term thermal stability tests indicated significant weight losses after 20 h of exposure at the temperature of 333∞C. Among the ionic liquids investigated, [$C_8$mim]$PF_6$ and [$C_4$mim][$Tf_2$N] were found to be the more thermally stable. The corrosivity of ionic liquids against 316 stainless steel and 1018 carbon steel was investigated at room temperature. Both Tafel plots and polarization curves were used to characterize corrosion behavior of the alloys in ionic liquids. The alloys were found to exhibit outstanding resistance to uniform corrosion.

**4:50 PM**
**Mutual Effects of Electro Slag Remelting and Open Die Radial Forging on the Properties of V-Microalloyed Steel**: *Taha MohamedTaha Mattar*[1]; [1]CMRDI, Steelmaking, PO Box 87, Helwan, Cairo 11421 Egypt

Both electro-slag remelting (ESR) and forging processes have a pronounced effect on the steel properties. ESR process as a refining process improves the cleanliness, soundness, homogeneity of alloying elements, and consequently the properties of steel. At the same time, metal forming processes are usually carried out not only for dimensional purposes but also enhancing the mechanical properties of steel. Better properties are obtained through grain refining of a desired microstructure. The present work aims at studying the mutual effects of both ESR using different refining slag compositions and open die radial forging process on the mechanical properties and structure of V-microalloyed steel. In this study V-HSLA steel consumable electrodes were produced in an electric arc furnace (EAF). These electrodes were electro-slag remelted into ingots of 120 mm diameter. The ingots produced by ESR were subjected to open die radial forging in the temperature range 1200-800°C. Forging has been carried out to different amounts of reduction in cross-sectional area. The forged bars were subjected to both mechanical testing and microstructure investigations. The obtained data showed pronounced improvements in the microstructure and mechanical properties upon controlling ESR slag composition and amount of reduction in cross-sectional area.

**5:10 PM**
**Quantitative Investigation of Hydrogen-Induced Additive Stress in Steel**: *Wuyang Chu*[1]; [1]University of Science and Technology Beijing, Dept. of Matls. Physics, Haidianqu Xueyuan lu No. 30, Beijing 100083 China

The flowing stress of a high-strength steel before unloading is different with the yield stress of the same sample extended in air after unloading and charging with hydrogen. The difference is the hydrogen-induced additive stress, which can help the applied stress to enhance the plastic deformation. The hydrogen-induced additive stress, Sigama(ad), induced through being immersed in a 3.5% NaCl solution with pH=4 increases linearly with the yield strength of the sample, e.g., Sigama(ad)=-106.6+0.14Sigama(ys). On the other hand, hydrogen-induced additive stress increases linearly with the logarithm of hydrogen concentration in the samples with the yield strengths of 900 and 1050MPa, i.e., Sigama(ad)=-55.5+63.6lnC0(Sigama(ys)=900MPa) and Sigama(ad)=-23.5+64.2lnC0(Sigama(ys)=1050MPa). To sum up, the hydrogen-induced additive stress is Sigama(ad)=-260+0.226Sigama(ys)+63.9lnC0.

## Global Development of Copper and Gold Deposits - II

*Sponsored by:* Extraction & Processing Division, EPD-Process Mineralogy Committee, EPD-Precious Metals Committee
*Program Organizers:* Tzong T. Chen, CANMET, Ottawa, Ontario K1A 0G1 Canada; Corby G. Anderson, Montana Tech of the University of Montana, Center for Advanced Mineral & Metallurgical Processing, Butte, MT 59701-8997 USA; Steven L. Chryssoulis, Amtel, London, Ontario N6G 4X8 Canada

Tuesday PM — Room: 1B
March 4, 2003 — Location: San Diego Convention Center

*Session Chairs:* Stephen Chryssoulis, Amtel, London, Ontario N6G 4X8 Canada; James Y. Hwang, Michigan Technological University, Inst. of Matls. Procg., Houghton, MI 49931-1295 USA

**2:30 PM**
**Removal and Recovery of Tellurium/Selenium from Copper Slimes Leachate**: *Shijie Wang*[1]; Brad Wesstrom[1]; Jean Fernandez[1]; [1]Phelps Dodge Mining Company, El Paso Ops., 6999 N. Loop Dr., El Paso, TX 79915 USA

In pressure oxidation leaching of copper anode slimes, more than 65% of the tellurium is co-extracted during decopperizing. About 10-15% of the selenium is also dissolved simultaneously by severe leach conditions. Current operation for the treatment of the leachate is to constantly recirculate the leach solution through a bed of copper turnings. The tellurium and selenium are precipitated from the leach liquor as copper telluride and copper selenide and separated from the solution by filtration. In order to improve the reaction efficiency and reduce the process cost, viz. minimize the copper addition, cut retention time, and reduce the energy consumption; a chemical reducing agent is studied and the cementation process tested in the laboratory. In this paper, the test results are presented and the process chemistry is discussed.

**3:00 PM**
**Characterization of Copper Vermiculite Antibacterial Nanomaterial**: Bowen Li[1]; Xiaodi Huang[1]; Zhiyong Xu[1]; *J. Y. Hwang*[1]; [1]Michigan Technological University, Inst. of Matls. Procg., 1400 Townsend Dr., Houghton, MI 49931-1295 USA

Silver, copper, and zinc are elements with good antibacterial and antifungal capabilities. Copper vermiculite has been prepared by ion exchange method. The antibacterial and antifungal properties of the prepared products have been demonstrated. Chemical and mineralogical characterization of the material is provided in this study.

**3:30 PM**
**Reducing the Calcium Hydroxide Consumption in Copper Flotation**: *Cristiano Zanforlin*[1]; Richard Araya[2]; [1]Cal Itau-Votorantim Group, Av. Dr. Jorge Dias de Oliva, 3301, Sao Jose da Lapa-Minas Gerais CEP: 33.350-000 Brazil; [2]Codelco Chile

Reducing costs in the flotation process is an important issue for the copper industry. However it commonly focuses the attention only on the chemical products which are more value added like flocculants or depressors. In spite of playing an important role in the flotation process, calcium hydroxide has never been subject of studies. Calcium hydroxide is used to correct the pH in the flotation in order to depress the pyrite from the copper ore. It is obtained by slaking the quicklime in water. The purpose of this work is investigating the performance of a quicklime developed for flotation process, the Flotlime Series\@. The product was approved in lab and pilot plant tests by Codelco-Chile, and then were conduced plant trials in El Teniente, Andina and Chuquicamata. The quicklime consumption was reduced in 40% and was observed an increase in molybdenum recovery.

**4:00 PM**
**Diagnostic Metallurgy of Porphyry Copper Ores**: *Joo Kim*[1]; [1]120 Pendennis Dr., Pointe-Claire, QC H9R 1H6 Canada

The processing of porphyry copper ores is highly variable mostly due to differences in ore mineralogy and nature of oxidations. Statistically designed flotation experiments were carried out with a number of different porphyry ores around the world to correlate the mineralogical significances to the metallurgical prediction. Various option of processing porphyry ores, such as flotation, gravity concentration and cyanidation are considered singularly or in combination with one another.

**4:30 PM**
**Bio-Oxidation of Arsenic-Bearing Gold Ores in China**: *Yang Hongying*[1]; Yang Li[2]; He Yongjun[2]; Fan Youjing[1]; Wang Junfeng[2]; [1]Northeastern University, Shenyang 110006 China; [2]Shandong Tarzan Bio-Gold Company, Ltd., Laizhou 261441 China

Many arsenic-bearing gold deposits have been found recently in China. The ores are treated using biological, roasting, or pressure-oxidation techniques, with bio-oxidation considered the best processes. Bio-oxidation plants of 50 t/d to 100 t/d have been built in Yantai and Laizhou, Shandong province during 2000 to 2001. The plants treat arsenic-bearing gold concentrates which contain 4-6% As, and gold recoveries are over 95%. Also, several companies in Shaanxi apply heap leaching technology to treat the ores. However, because of possible arsenic pollution, most arsenic-bearing gold deposits in China have not been exploited. The Chinese government now promotes the ìfriendly environmental metallurgyî; consequently, it is expected that bio-oxidation technology will become more important for treating arsenic-bearing gold ores.

**5:00 PM**
**Effects of Roasting Conditions on Copper and Zinc Ferrites ($CuFe_2O_4$, $Cu_xZn_{1-x}Fe_2O_4$ and $ZnFe_2O_4$), Production and an Investigation on Parameters Affecting Cuo and Zno Co-Leacheability**: *A. F. Mulaba-Bafubiandi*[1]; [1]Technikon Witwatersrand, Rsrch. Dvlp. Unit, Fac. of Eng., PO Box 526, Wits, Johannesburg 2050 S. Africa

In the hydrometallurgy of zinc, copper and zinc are generally extracted from calcine produced by roasting zinc-copper sulphides concentrate. The concentrate in a form of sulphides is subjected to high temperature conditions to convert the sulphides into oxides. The resulting calcine contains copper and zinc in a form of copper oxide (CuO), zinc oxide (ZnO), copper sulphate ($CuSO_4$), zinc sulphate ($ZnSO_4$), and copper and zinc ferrites $CuFe_2O_4$, ($Zn_{1-x}$, $Cu_x$)$OFe_2O_3$, and ($ZnFe_2O_4$), ferrites being co-produced during the high temperature roasting process. Their insolubility in relatively dilute sulphuric acid and low temperatures results in a significant amount of zinc and copper remaining in the residue. Zinc ferrite and copper ferrite are therefore sources of metal loss. The ferrite formation has been scrutinized in order to minimize their formation. XRD, the sulphur removal test and Mˆssbauer spectroscopy were used to study the optimization process. A relatively dead roasting was achieved at 900°C for 3 hours. At 800°C Copper and zinc oxides (CuO and ZnO) formation dominated over the competing zinc ferrite and other ferrites (copper ferrite). Mˆssbauer results show the ferrites in different forms with hyperfine interactions parameter values confirmed by the literature (Stevens, et. al, 1998). Their abundances are found to depend on the roasting conditions. The rate of hematite formation decreased with increase in temperature and on the contrary, the ferrites were forming with increase in temperature. The optimum temperature was achieved at 800°C for 3 hours. Results on the optimisation of the roasting process were published somewhere else (Sibiya-Magagula and Mulaba-Bafubiandi, 2002). Leaching experiments were done using three different acids (HCl, $H_2SO_4$ and $HNO_3$) at 50°C and later at 90°C using mild (15g/l) and strong (55g/l) concentrations respectively. The HCl resulted in the highest percentage extraction of all the metals. Above 90% of copper was extracted from neutral leach and a percentage of only 80-85 for iron and zinc could be extracted from neutral leach. References: 1. J.G. Stevens, A.M. Khasanoy, J.W. Miller, H. Pollak and Z.Li. Mˆssbauer Mineral Handbook. Mˆssbauer Effect Data Centre, 1998. F.N. Sibiya-Magagula and A.F Mulaba-Bafubiandi, SAIMM Proceedings, July 2002.

## Hot Deformation of Aluminum Alloys: Superplasticity and Creep

*Sponsored by:* Materials Processing and Manufacturing Division, MPMD-Shaping and Forming Committee
*Program Organizers:* Zhe Jin, Alcoa Technical Center, Thermomechanical Processing and Alloy Development, Alcoa Center, PA 15069 USA; Armand J. Beaudoin, University of Illinois at Urbana-Champaign, Department of Mechanical and Industrial Engineering, Urbana, IL 61801 USA; Thomas R. Bieler, Michigan State University, Department of Chemical Engineering and Materials Science, East Lansing, MI 48824-1226 USA; Balasubramaniam Radhakrishnan, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6359 USA

Tuesday PM — Room: 6E
March 4, 2003 — Location: San Diego Convention Center

*Session Chairs:* Terence G. Langdon, University of Southern California, Depts. of Aeros. & Mechl. Eng. & Matls. Sci., Los Angeles, CA 90089-1453 USA; Rajiv S. Mishra, University of Missouri, Dept. of Metallurgl. Eng., Rolla, MO 65409 USA

**2:00 PM Invited**
**Creep and Superplasticity in Aluminum Alloys**: *Farghalli A. Mohamed*[1]; [1]University of California, Dept. of Cheml. Eng. & Matls. Sci., 916 Eng. Tower, Irvine, CA 92697-2575 USA

It is well-documented that trace levels of impurities, solute atoms, precipitates, and dispersion particles play an important role in the deformation and fracture of polycrystalline materials. At temperatures above about 0.5 Tm, where Tm is the melting point of the material, this role is reflected in several phenomena that include the segregation of impurities at boundaries, the occurrence of viscous glide creep, and the introduction of a threshold stress for creep in dispersion strengthened (DS) alloys. This paper provides recent examples that demonstrate the role of trace elements, solute atoms, and dispersion particles in modifying high-temperature deformation of aluminum and its alloys. These examples deal with creep in powder metallurgy (PM) Al alloys, very low-stress creep behavior in Al, and superplastic flow in Zn-22% Al.

**2:25 PM**
**Creep Properties of Heat-Treatable Al-Mg-Sc Alloys at 300∞C**: *Emmanuelle A. Marquis*[1]; David N. Seidman[1]; David C. Dunand[1]; [1]Northwestern University, Matls. Sci. & Eng. Dept., 2225 N. Campus Dr., Evanston, IL 60208-3108 USA

A study of the creep properties at 300∞C of precipitation-strengthened Al-Sc alloys containing Mg in solid solution is presented. Threshold stresses were measured in the range of 0.09sOr to 0.6sOr, where sOr is the Orowan stress. At large applied stresses, the creep strength is significantly improved as compared to binary Al-Sc alloys, and is independent of the size of the Al3Sc precipitates with a stress exponent close to 5. To study the effect of precipitate dimensions on the threshold stress, aging treatments were varied to form Al3Sc precipitates with average radii ranging from 2 to 30 nm. The effect of coherency state of the matrix/precipitate interface was also investigated, as precipitates lose coherency for radii larger than ~12 nm. Existing models for climb-controlled bypass mechanisms are extended to describe the precipitate radius dependence of the measured threshold stresses, as well as the effect of dislocations at the precipitate interfaces.

**2:45 PM Invited**

**High Strain Rate Superplasticity of Metal Matrix Composites**: *Tsunemichi Imai*[1]; Naofumi Saito[1]; Shangli Dong[1]; [1]National Institute of Advanced Industrial Science & Technology, Inst. of Structl. & Eng. Matls., 2266-98 Shimoshidami, Moriyama-ku, Nagoya 463-8650 Japan

Hot-rolling after extrusion are used as thermomechanical processing to build fine grain size in matrix, to control interface between matrix and reinforcement and to disperse reinforcement uniformly for Metal Matrix Composites(MMC) and the high strain rate superplasticity (HSRS) of MMC is investigated. (1) Pure aluminum (1N90) fabricated by PM method exhibits maximum total elongation more than 500% and at the strain rate of 10-2s-1 and at 893K, which is below of melting temperature of pure aluminum. And TiN/1N90, TiC/1N90 and AlN/1N90 indicate about 200% elongation at the strain rate of 10-1s-1 and at 913K. It is thought, therefore, that HSRS could produce by fine grain boundary sliding and accommodation mechanism with dislocation movement. (2) TiN/2124, TiC/2124 and AlN/6061 Al composites exhibits larger total elongation of 300~500% at the strain rate of 10-0s-1 and above solidus temperature of matrix alloys so that these composites could produce HSRS by interfacial sliding with partial melting phase in addit ion with grain boundary sliding. (3) Also nitrided mullite short fiber reinforced 60661 Al composites produces HSRS because mullite short fibers are covered by Sialon particle on the surfaces and Sialon is available to avoid reaction of mullite with magnesium.

**3:10 PM**

**High Strain Rate Superplastic Deformation of 30 vol.% AlNp/6061Al Composite**: *Lihong Han*[1]; Jitai Niu[2]; Henry Hu[1]; [1]University of Windsor, Dept. of Mechl., Auto. & Matls. Eng., Windsor, Ontario N9B 3P4 Canada; [2]Harbin Institute of Technology, Sch. of Matls. & Tech. Eng., Harbin, Hei Long Jiang 150001 China

The superplasticity of 30 vol.% AlN particulate-reinforced 6061Al composite, prepared by Powder Metallurgy techniques (PM), was investigated. In this study, superplastic tensile tests of the composite were carried out at strain rates ranging from 100-10-3 s-1 and at temperatures from 823K to 893K. Hot rolling of the composite after extrusion was employed to obtain a fine-grained structure prior to superplastic testing. More than 300% total elongation was achieved at a temperature of 853~873 K and at an initial strain rate of 1.67x10-1 s-1. The results indicate that the highest value of the strain rate sensitivity index (m) is 0.42 for the composite. A differential scanning calorimeter (DSC) was used to ascertain the possibility of any partial melting in the vicinity of optimum superplastic temperatures. Microstructure and fracture behavior of the composite were examined with a Scanning Electronic Microscope. Characteristics of the interface between the reinforcement and the matrix were also investigated by using a Transmission Electronic Microscope.

**3:30 PM Invited**

**Review of Current Commercial Applications for High Strain Rate Superplastic Aluminum Alloys**: *Kenji Higashi*[1]; *Toshiji Mukai*[2]; [1]Osaka Prefecture University, Dept. of Metall. & Matls. Sci., 1-1, Gakuen-cho, Sakai, Osaka 599-8531 Japan; [2]Osaka Municipal Technical Research Institute, 1-6-50 Morinomiya, Joto-ku, Osaka 536-8553 Japan

Superplasticity is a viable technique to fabricate a hard-to-form material into complex shape. The detailed feature has been investigated in the past two decades. The limitation to apply for commercial mass-production is the low optimum forming speed and the material cost. One of the innovations in superplasticity is especially noted to establish the high strain rate superplasticity(HSRS) in early 1990s. Detailed study of the phenomenological aspect in HSRS revealed its deformation mechanism and pointed out the importance of the presence of accommodation helper such as discontinuous liquid phase with grain boundary sliding. Recently, HSRS has been applied for net-shape forging of engine piston with rapidly-solidified Al-Si system alloy powders. Another commercial application of HSRS is gas-pressure forming of Al-Mg system alloys to produce large scale components, i.e., constructing outer parts, roof of automobiles. In this study, we discuss the phenomenological deformation mechanism of HSRS in aluminum alloys and review of the current applications in Japan.

**3:55 PM**

**Characterization of Superplastic Response in Al-Mg Alloys**: *P. A. Friedman*[1]; W. Copple[1]; [1]Ford Research Laboratory, 2101 Village Rd., MD 3135, Dearborn, MI 48121 USA

The ability to achieve large strains to failure coupled with extremely low flow stresses makes superplastic forming an attractive option in the automotive industry for the manufacture of complex parts from aluminum sheet. However, a barrier to increased usage is the cost penalty associated with alloys that are specially processed to have a small and stable grain size which makes them suitable for superplastic forming. In this paper, a series of elevated-temperature tensile tests are used to characterize the superplastic response of Al-Mg alloys that were specially processed for superplastic forming as well as an alloy which was conventionally processed. Results from these tensile tests coupled with optical microscopy are used to both establish the superplastic forming potential of these alloys as well as to highlight the different mechanisms that control deformation in the two types of materials.

**4:15 PM**

**Thermo-Mechanical Process Optimization for Enhancing Superplastic Ductility of 5083 Aluminum Sheet**: *Ravi Verma*[1]; [1]General Motors, Matls. & Processes Lab., 30500 Mound Rd., Warren, MI 48090 USA

Effect of sheet rolling practice on superplastic response of 5083 aluminum alloy has been investigated. A synergistic effect between hot rolling and cold rolling processes has been observed, which helps optimize an efficient sheet rolling practice for producing superplastic sheet. In addition, a iskewedî cold-rolling practice is proposed in which successive rolling reduction levels are tailored to maximize the alloyís hardening response to cold work. This optimized cold rolling practice increases the amount of work introduced into the sheet (as measured by sheet hardness) for a given net gauge reduction, and thereby improves the superplastic response of the 5083 sheet on recrystallization. Superplastic ductility values greater than 400% have been obtained with the optimized rolling practice.

**4:35 PM**

**Superplasticity in a Commercial Al-Mg-Mn-Sc Alloy Subjected to Intense Plastic Straining**: *Fanil Musin*[1]; Rustam Kaibyshev[2]; Yoshinobu Motohashi[1]; [1]Ibaraki University, Rsrch. Ctr. for Superplasticity, Nakanarusawa-cho, 4-12-1, Hitachi, Ibaraki 316-8511 Japan; [2]Institute for Metals Superplasticity Problems, Khalturina str., 39, Ufa 450001 Russia

The superplastic behavior of an Al-5.76%Mg-0.3%Mn-0.32%Sc alloy (1570 Al) subjected to intense plastic straining by equal-channel angular extrusion (ECAE) was studied in the temperature interval 200-500°C at strain rates ranging from $1.4x10^{-5}$ to $1.4\ s^{-1}$. The grain size after ECAE was about 1μm. The highest elongation to failure of 2000% was recorded at a temperature of 450°C and initial strain rate of $5.6x10^{-2}\ s^{-1}$ with corresponding coefficient of the strain rate sensitivity of 0.6. It was shown that the ECAE processed 1570 Al exhibits superior superplastic properties in the temperature range 300-500°C with the strain rate sensitivity higher than 0.4. Microstructural evolution and cavitation during high strain rate superplastic deformation were examined.

**4:55 PM**

**Achievement of High Superplastic Properties of Al-Mg-Si Alloys in Partially Melted State**: *Rustam Kaibyshev*[1]; Fanil Musin[1]; Dmitry Gromov[1]; T. G. Nieh[2]; Donald R. Lesuer[2]; [1]Institute for Metals Superplasticity Problems, Khalturina str., 39, Ufa 450001 Russia; [2]Lawrence Livermore National Laboratory, L-342, PO Box 808, Livermore, CA 94551 USA

The superplastic properties of a commercial grade of 6061 aluminum alloy (6061Al) and a modified (0.15%Zr-0.7%Cu) 6061Al were examined in tension at T=475-620∞C and at a strain rate range of $7x10^{-6}$-$2.8x10^{-2}s^{-1}$. The same two-step thermomechanical processing was used to obtain the refined microstructure in both alloys. It was shown using differential thermal analysis that the highest superplastic characteristics were obtained in partially melted state. The modified 6061Al exhibited a maximum elongation-to-failure of 1300% at 590∞C and at a strain rate of $2.8x10^{-4}s^{-1}$. In contrast, the highest total elongation of 350% was achieved in the commercial grade 6061Al at 600∞C and at a strain rate of $1.4x10^{-4}s^{-1}$. Significant enhancement of the superplastic properties of the modified 6061Al in partially melted state was provided by optimum amount of liquid phase contributing proper accommodation of grain boundary sliding as well as by essential stability of the fine-grained structure with $Al_3Zr$ dispersoids.

## International Symposium on Gamma Titanium Aluminides: Environmental Effects and Applications

*Sponsored by:* Structural Materials Division, ASM International: Materials Science Critical Technology Sector, ASM/MSCTS-Materials & Processing, SMD-High Temperature Alloys Committee, SMD-Titanium Committee

*Program Organizers:* Young-Won Kim, UES, Inc., Materials & Processes Division, Dayton, OH 45432 USA; Helmut Clemens, GKSS, Institute of Materials Research, Geesthacht D-21502 Germany; Andrew H. Rosenberger, Air Force Research Laboratory, Materials & Manufacturing Directorate, Wright-Patterson AFB, OH 45433-7817 USA

Tuesday PM　　Room: 6F
March 4, 2003　　Location: San Diego Convention Center

*Session Chairs:* Andrew H. Rosenberger, Air Force Research Laboratory, Matls. & Mfg. Direct., WPAFB, OH 45433-7817 USA; Shigehisa Naka, ONERA, Materiaux Metalliques et Procedes, Chatillon Cedex 92322 France

TUESDAY PM

**2:00 PM Invited**

**Oxidation Resistance of γ-TiAl Based Alloys in a Simulated Combustion Atmosphere**: *Shigeji Taniguchi*[1]; Xiangyang Li[1]; [1]Osaka University, Matls. Sci. & Procg., 2-1 Yamadaoka, Suita, Osaka 565-0871 Japan

The cyclic oxidation behaviour of the γ-TiAl based alloys, Ti-48Al-2Cr-2Nb, Ti-48Al-2Cr-2Fe, Ti-48Al-2Cr-2W and Ti-48Al-2Cr-1W-1Ta (at. %), was examined in a simulated automobile exhaust gas at 1123 K for up to 1080 ks (300 h) to evaluate their practical performance under aggressive environment. The oxidation products were identified by XRD and the microstructure, elemental constitution of the oxide scale were characterized by SEM and EPMA. The effects of the alloying element on the oxidation resistance were discussed on the basis of above evidence. The alloys except Ti-48Al-2Cr-2Fe showed excellent oxidation resistance for at least 15 cycles (300 h) in which Ti-48Al-2Cr-2W gives the best performance followed by Ti-48Al-2Cr-1W-1Ta and Ti-48Al-2Cr-2Nb. The alloy additions of W, Ta and Nb could enhance the cyclic oxidation resistance of TiAl alloy in simulated exhaust gas and Fe shows detrimental effect. Further investigation indicated that alloying elements such as W, Ta and Nb played a significant role in promoting the primary oxidation of Al, namely resulted in large amounts of alumina in the oxide scale and eventually led to the overall low growth rate and strong oxidation resistance.

**2:30 PM**

**Environmental Protection of Gamma Titanium Aluminides**: *Christoph Leyens*[1]; Reinhold Braun[1]; Papken Eh. Hovsepian[2]; Wolf-Dieter M¸nz[2]; [1]DLR-German Aerospace Center, Inst. of Matls. Rsrch., Linder Hoehe, Cologne D-51170 Germany; [2]Sheffield Hallam University, Matls. Rsrch. Inst., City Campus, Howard St., Sheffield S1 1WB UK

The current development of new generation gamma titanium aluminides is expected to result in alloy chemistries and microstructures capable of resisting temperatures well in excess of 850∞C. Under these conditions, environmental and thermal protection becomes a concern since oxidation and wear/erosion might eventually limit the maximum service temperatures achievable. In the present paper, two approaches will be highlighted. Advanced nitride coatings based on the Ti-Al-Cr-Y-N system have demonstrated excellent oxidation resistance under isothermal and cyclic conditions up to 900∞C in long-term tests of several thousand hours. In addition to oxidation resistance these coatings provide excellent wear protection. Along with the oxidation data a detailed microstructure analysis before and after testing will be presented demonstrating the thermal stability and integrity of the coatings. Furthermore, EB-PVD thermal barrier coatings applied to gamma titanium aluminides will be highlighted. The TBCs survived 1000 h at 850 and 900∞C without failure before the tests were terminated. Microstructure analysis will emphasize the outstanding performance of the coatings.

**2:50 PM**

**The Oxidation Behavior of Engineering Gamma TiAl Alloys**: *Michiko Yoshihara*[1]; Young-Won Kim[2]; [1]Yokohama National University, Mechl. Eng. & Matls. Sci., 79-5 Tokiwadai, Hodogaya-ku, Yokohama, Kanagawa 240-8501 Japan; [2]UES, Inc., Matls. & Processes, 4401 Dayton-Xenia Rd., Dayton, OH 45432 USA

The present paper is a part of continuing work concerning the oxidation behavior of engineering gamma TiAl alloys under development. The gamma alloys have attractive properties as light weight heat resistant structural materials, however the oxidation resistance of them at elevated temperatures is not enough. For practical applications, it is important to understand the oxidation behavior of the alloys. This paper provides recent knowledge about the oxidation resistance of the gamma alloys in air, with isothermal exposure at 870∞C up to 200h as well as two hours cyclic exposure at 760∞C, 815∞C and 870∞C up to 1000 hours. The materials tested include five cast alloys (K5C, 395E, K1A, K1B and K1C) and seven forged alloys (95D, K5A, 395N, 98B, 99B, 99D and 99G). The alloy with high Nb content showed good oxidation behavior, however other alloying elements also have some influences on oxidation behavior. Detailed results will be discussed.

**3:10 PM**

**Development of Oxidation Resistant Coatings Based on Gamma TiAl**: *Panos Tsakiropoulos*[1]; Antonis Zaroulias[1]; Guosheng Shao[1]; [1]University of Surrey, Sch. of Eng., Mechl., Matls. & Aeros. Eng., Guildford, Surrey GU2 7XH UK

The development of gamma TiAl base alloys has addressed their oxidation and mechanical properties. The selected alloying additions to gamma and gamma + a2 alloys do not result in continuous Al2O3 scale formation in air. An intermixed Al2O3/TiO2 scale continues to form in the more complex alloys, but the rate of growth of this scale has been reduced. Alloys with Cr additions at a level generally above 8 to 10 at% can form a two-phase (gamma + Laves phase) microstructure and are capable of continuous Al2O3 scale formation in air. Furthermore, the Ti-Al-TM tau phases form protective Al2O3 in air, with the best oxidation behaviour exhibited by TM = Cr. Thus, the Ti-Al-Cr system offers unique opportunities for the design of coatings that are mechanically compatible with the substrate and also oxidation resistant. The paper will report results of our experimental study of Ti-Al-Cr coatings applied by PVD on gamma base substrates. The coatings have been designed for oxidation resistance using thermodynamic database s and microstructure models developed at the University of Surrey. A distinct feature of our study is the deposition of amorphous coatings with high crystallisation temperatures. The design and processing of coatings will be presented. The microstructures and properties of the as deposited and nanocrystalline coatings will be discussed.

**3:30 PM**

**Moisture-Induced Embrittlement of Isothermally Forged TiAl-Based Intermetallic Alloys with Various Kinds of Microstructures**: *Takayuki Takasugi*[1]; Yasuyuki Kaneno[1]; Hirofumi Inoue[1]; [1]Osaka Prefecture University, Dept. of Metall. & Matls. Sci., 1-1 Gakuen-cho, Sakai, Osaka 599-8531 Japan

Isothermally forged TiAl-based intermetallic with various microstructures (gamma grain, duplex, dual phase and fully lamellar microstructures) were prepared. These TiAl-based intermetallic alloys were tensile tested in vacuum and air as functions of strain rate and temperature. All intermetallic alloys and all microstructures showed reduced tensile strength (or elongation) in air at room temperature. The tensile strength (or elongation) of the specimens deformed in air tended to recover to the values of the specimens deformed in vacuum as temperature (or strain rate) increases. From the measured recovering temperatures, it was found that the gamma grain microstructure was the most resistive to the moisture-induced embrittlement, and the dual phase microstructure was the most susceptible to the moisture-induced embrittlement. Also, the moisture-induced embrittlement of the alloys with fully lamellar microstructure was reduced with decreasing lamellar spacing. The observed microstructural effect on the moisture-induced embrittlement was explained, in association with hydrogen properties and kinetics in the constituent phases and at some interfaces.

**3:50 PM Invited**

**Texture Formation in Gamma-TiAl**: *Arno Bartels*[1]; Helmut Clemens[2]; Wolfram Schillinger[1]; [1]TU Hamburg-Harburg, Matls. Sci. & Tech., Eissendorfer Str. 42, Hamburg D-21073 Germany; [2]GKSS-Research Centre, Inst. for Matls. Rsrch., Max-Planck-Str. 1, Geesthacht D-21502 Germany

Processing of gamma-TiAl based alloys like forging or rolling often results in strong textures, which lead to undesirable anisotropies of mechanical properties. To avoid these textures the knowledge of texture formation during processing is doubtless necessary. It will be shown that during deformation at high temperatures texture components formed comparable to those known from fcc-metals with low stacking fault energies. Due to the tetragonality of the crystalline structure these components are split with respect to the difference between a- and c-axes. Components predominantly formed by slip of superdislocations or by mechanical twinning are vanishing during recrystallization in the processing heat. After forging and rolling new recrystallization induced texture component occur with strong alignments of the [001]-directions resulting in anisotropies of the mechanical properties. To avoid these anisotropies the recrystallization process must be diminished by a special choice of processing parameters or by an alloy exhibiting a lower inclination to recrystallization.

**4:20 PM Invited**
**Titanium Aluminide Turbine Wheels for Turbocharger Applications**: *Stephen J. OíHara*[1]; [1]Caterpillar, Inc., Air Sys., 3701 State Rd. 26 E., Lafayette, IN 61656 USA

Internal combustion engine makers are pressed by legislation to develop and manufacture cleaner engines. At the same time they continue their drive for improved fuel consumption and competitive sales costs in order to maintain market share. Turbocharger technologies such as EGR; VGT; Series and Sequential machines play an ever increasing role in providing the engine maker with enhancements to the engine exhaust and air intake systems. The Titanium Aluminide turbine wheel offers the turbine designer a low mass, low inertia alternative to alloys such as Inconel 713C. In turn this would allow better high temperature materials such as Titanium to be used in the compressor section of the rotating group without increasing rotor inertia. The improved specific strength and stiffness of Titanium Aluminide may allow the designer more scope for Improved turbine design.

**4:50 PM Invited**
**Titanium Aluminides for Automotive Applications**: *Hartmut Baur*[1]; Daniel B. Wortberg[1]; Helmut Clemens[2]; [1]DaimlerChrysler AG, RBP/SM, Wilhelm-Runge-Str. 11, Ulm 89081 Germany; [2]GKSS Research Centre, Inst. for Matls. Rsrch., Max-Planck-Strafle, Geesthacht 21502 Germany

Titanium aluminides have proven their principle suitability for automotive applications. This paper evaluates the technical benefits of titanium aluminides for rotating and oszillating components based on first engine tests. These promising results on the one hand and the limited availability of high qualitative titanium aluminides components in acceptable quantities and at reasonable costs on the other hand have led to extensive research efforts. This paper summarizes the current state of titanium aluminides with regard to material properties, production process, quality and quality control of cast prototypes as well as cost situation. Critical points and the demand on future research and development will be outlined. These points will be elaborated on the basis of the potential use of titanium aluminides for turbocharger wheels. Besides this component possible other applications in automotive combustion engines will be presented. Finally, the strategy to promote titanium aluminides into series production will be discussed.

**5:20 PM**
**A Microstructural Study of the Fusion Zone of Gas Tungsten Arc Welded Gamma Titanium Aluminde**: Mario F. Arenas[1]; *Viola L. Acoff*[1]; [1]The University of Alabama, Dept. of Metallurgl. & Matls. Eng., Box 870202, Tuscaloosa, AL 35487-0202 USA

Although various studies have been performed on the weldability of gamma titanium aluminides, little is known about the microstructure that evolves during the gas tungsten arc welding process. This technique has been proposed for gamma repair operations due to its flexibility and relative cost-effectiveness. In this study cast, hot-isostatic pressed (HIPed) gamma titanium aluminides alloys of composition Ti-48Al-2Cr-2Nb were welded using GTAW without preheating. Microstructural examination revealed a nearly lamellar microstructure in the base metal which was transformed to dendritic with evidence of interdendritic gamma phase and metastable structures in the fusion zone. The solid state transformations that occurred were heavily dependent on the cooling rate. It was found that the selected welding parameters should ensure that the heat affected zone cooling rate will be less than 500 K/s. Such cooling rates prevent the development of deleterious alpha-2 structures, which promote cracking.

**5:40 PM**
**Microstructural Aspects of Diffusion Bonding of High Niobium Containing Gamma TiAl-Based Alloys**: *Cesar Justino Buque*[1]; Fritz Appel[1]; [1]GKSS Research Centre, Inst. of Matls. Rsrch., Max-Planck-Str. 1, Geesthacht 21502 Germany

The paper describes a detailed analysis of diffusion bonding (DB) of a Ti-45Al-10Nb (at.%) representing a new generation of TiAl alloys with enhanced high-temperature capability. The study involves scanning electron microscopy coupled with chemical microanalysis and electron backscattered diffraction. DB of this alloy results in the formation of $\alpha 2$(Ti3Al) grains at the bonding interface surrounded by $\gamma$(TiAl) grains. In few cases the formation of $\beta$/B2 small particles was also found. Nucleation of the $\alpha 2$ grains occurs at the expense of the $\alpha 2$ lamellae and probably involves migration of antisite defects via antistructural bridges. Remnant deformation structures and the occurrence of a {10-10}-texture of the $\alpha 2$ grains suggest that the recrystallisation processes are driven by localised deformation. These results will be compared with those found by DB of binary alloys with regard to the basic mechanisms involved and discussed with respect to the optimisation of bonding parameters towards improved bond strengths.

## International Symposium on Intermetallic and Advanced Metallic Materials - A Symposium Dedicated to Dr. C. T. Liu: Intermetallics IV–Bulk Metallic Glasses

*Sponsored by:* ASM International: Materials Science Critical Technology Sector, Structural Materials Division, SMD-Mechanical Behavior of Materials-(Jt. ASM-MSCTS)
*Program Organizers:* Seetharama C. Deevi, Philip Morris USA, Research Center, Richmond, VA 23234 USA; Fritz Appel, GKSS Research Centre, Geesthacht D-21502 Germany; Robert W. Cahn, University of Cambridge, Materials Science and Metallurgy, Cambridge CB2 3QZ UK; Y. Austin Chang, University of Wisconsin-Madison, Department of Materials Science & Engineering, Madison, WI 53706-1595 USA; Guo Liang Chen, University of Science and Technology-Beijing, State Key Laboratory for Advanced Metals and Materials, Beijing 100083 China; Yip-Wah Chung, Northwestern University, Department of Materials Science & Engineering, Evanston, IL 60208-3108 USA; Shuji Hanada, Tohoku University, Sendai 980-8577 Japan; Linda Horton, Oak Ridge National Laboratory, Metals and Ceramics Division, Oak Ridge, TN 37831-6132 USA; Peter K. Liaw, University of Tennessee, Department of Materials Science and Engineering, Knoxville, TN 37996-2200 USA; Dong-Liang Lin, Shangai Jiao-Tong University, Shangai 200030 China; T. G. Nieh, Lawrence Livermore National Laboratory, Livermore, CA 94551 USA; Masaharu Yamaguchi, Kyoto University, Department of Materials Science & Engineering, Kyoto 606-8501 Japan

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| Tuesday PM | Room: 8 |
| March 4, 2003 | Location: San Diego Convention Center |

*Session Chairs:* Shuji Hanada, Tohoku University, Inst. for Matls. Rsrch., Sendai 980-8577 Japan; Peter K. Liaw, University of Tennessee, Dept. of Matls. Sci. & Eng., Knoxville, TN 37996-2200 USA

**2:00 PM Invited**
**Nanoscratch of Metallic Glasses**: *T. G. Nieh*[1]; Jessica Lensch[2]; Chris Schuh[3]; [1]Lawrence Livermore National Laboratory, L350, PO Box 808, Livermore, CA 95014 USA; [2]Carnegie Mellon University, Matls. Sci. & Eng., Pittsburgh, PA 15213 USA; [3]Massachusetts Institute of Technology, Matls. Sci. & Eng., 77 Massachusetts Ave., Cambirdge, MA 02139 USA

The tribological and wear behavior of several bulk metallic glasses, including Zr-, Pd-, La-, and Ti-based materials, was investigated. These materials, in both the as-cast and annealed states, were tested using nano-scratch tests, specifically using ramping load scratch techniques. Mechanical properties, such as Youngís modulus, hardness, friction coefficient, and tribological wear were measured. These properties were found to vary with microstructure. An increase in annealing temperature causes an increase in hardness and reduces wear. Samples having a structure consisting of nanocrystals within the amorphous matrix exhibit an improved wear performance. Also, the wear resistance was found to follow the conventional Archardís equation for dry wear, specifically, the volume of material removed by wear is inversely proportional to the hardness of a material. In the present study, special efforts were made to study the wear rate as a function of scratch rate. This work was performed under the auspices of the US Department of Energy (DOE) under contract No. W-7405-Eng-48 with Lawrence Livermore National Laboratory.

**2:20 PM Invited**
**Fatigue Behavior of Bulk Metallic Glasses**: *P. K. Liaw*[1]; G. Y. Wang[1]; W. H. Peter[1]; B. Yang[1]; Y. Yokoyama[2]; M. L. Benson[1]; B. A. Green[1]; M. J. Kirkham[1]; S. A. White[1]; T. A. Saleh[1]; R. L. McDaniels[1]; R. V. Steward[1]; R. A. Buchanan[1]; C. T. Liu[3]; C. R. Brooks[1]; [1]The Univer-

sity of Tennessee, Dept. of Matls. Sci. & Eng., TN 37996 USA; [2]Himeji Institute of Technology, Matls. Sci. & Eng., Shosha, Himeji City 2167 Japan; [3]Oak Ridge National Laboratory, Metals & Ceram. Div., Oak Ridge, TN 37831 USA

High-cycle fatigue (HCF) experiments were conducted on zirconium (Zr)-based bulk metallic glasses (BMGs): Zr-10Al-40Cu, Zr-10Al-30Cu-10Ni, and Zr-10Al-5Ti-17.9Cu-14.6Ni, in atomic percent. The HCF tests were performed using an electrohydraulic machine at a frequency of 10 Hz with a R ratio of 0.1 and under tension-tension loading. Note that R = smin./smax., where smin. and smax. are the applied minimum and maximum stresses, respectively. The test environments were air and vacuum. A high-speed and high-sensitivity thermographic infrared (IR) imaging system was used for nondestructive evaluation of temperature evolution during fatigue testing of BMGs. Limited temperature evolution was observed during fatigue. The effect of chemical composition on the fatigue behavior of the Zr-based BMGs was studied. The fatigue life in vacuum was generally found to be shorter than in air. The dissociation of residual water vapor to atomic hydrogen in vacuum via a hot-tungsten-filament ionization gauge, and subsequent hydrogen embrittlement of BMGs, could have been a factor causing the lower fatigue lifetimes observed in vacuum. The fatigue resistance of Zr-10Al-40Cu and Zr-10Al-30Cu-10Ni seemed not to be as good as that of Zr-10Al-5Ti-17.9Cu-14.6Ni. The fatigue endurance limit of Zr-10Al-5Ti-17.9Cu-14.6Ni was found to be at least comparable to those of structural materials. The cracking shapes on the fatigue surfaces were analyzed and predicted. The present work is supported by the National Science Foundation (NSF) Integrative Graduate Education and Research Training (IGERT) Program with Drs. P. W. Jennings and L. S. Goldberg as contract monitors.

**2:40 PM Invited**
**Toughness of Metallic Glass and Bulk Metallic Glass**: *John J. Lewandowski*[1]; Peravudh Lowhaphandu[1]; Paul Wesseling[1]; [1]Case Western Reserve, Dept. Matls. Sci. & Eng., Cleveland, OH 44106 USA

The toughness of metallic glass materials is being measured under a number of different test conditions. The effects of changes in notch root radius on the toughness are being determined in addition to determining the effects of changes in loading rate and test temperature on both amorphous and partially devitrified glasses. The results will be reviewed in the light of ongoing work on such materials. P. Lowhaphandu/JJ Lewandowski, Scripta Metall et Mater., 38,12, 1811-1817, 1998. P. Lowhaphandu, LA Ludrosky, SL Montgomery and JJ Lewandowski, Intermetallics, 8, 487-492, 2000. JJ Lewandowski, Materials Transactions-JIM, 42(4), 633-637, 2001.

**3:00 PM**
**Fracture and Deformation of Bulk Metallic Glasses and their Composites**: *Katharine M. Flores*[1]; Reinhold H. Dauskardt[1]; [1]Stanford University, Dept. of Matls. Sci. & Eng., 416 Escondido Mall, Bldg. 550, Stanford, CA 94305-2205 USA

Combining low density, large elastic strains, high strength, and a high fracture toughness, bulk metallic glasses represent an exciting new class of materials with a wide range of potential applications. Plastic deformation of metallic glasses occurs by the formation of shear bands, however, the role of free volume magnitude and distribution, the effects of adiabatic heating and stress state, and the extent of local structural rearrangement are under active investigation. In this work, we investigate the mode II deformation and fracture behavior of a zirconium-based bulk metallic glass. The mode II fracture toughness was found to be ~75 MPa√m, ~4-5 time larger than the mode I toughness. This may be explained by the sensitivity of flow to normal stresses. The fracture and fatigue behavior of a BMG composite utilizing ductile particle reinforcement phases has been examined and compared with that of the monolithic alloy. The second phase blocks the propagation of shear bands and distributes the plastic defo rmation, resulting in extensive stable crack growth at stress intensities double the intrinsic toughness of the unreinforced glass. The composite also exhibits an improved fatigue endurance. Implications for future composite microstructures are discussed.

**3:15 PM**
**Consolidation of Zirconium Based Metallic Glass Powder by Equal Channel Angular Extrusion**: *K. T. Hartwig*[1]; I. Karaman[1]; J. Robertson[1]; S. N. Mathaudhu[1]; J.-T. Im[1]; I. E. Anderson[2]; [1]Texas A&M University, Dept. of Mech. Eng., College Station 77843-3123 USA; [2]Iowa State University, Ames Lab., Ames, IA 50011 USA

Vitreloy 106a (Zr58.5Nb2.8Cu15.6Ni12.8Al10.3) gas-atomized powder was consolidated by equal channel angular extrusion (ECAE). Vacuum encapsulated powder was extruded at temperatures above the glass transition temperature ($T_g$) but below the crystallization temperature ($T_x$). The oxygen level in the powder is measured to be approximately 1300 ppmw. Microstructure, thermal stability, X-ray diffraction measurements and hardness of the ECAE consolidates were examined and compared with those of the initial powder. The effects of strain rate and consolidation temperature on the consolidation quality and resulting properties were investigated. Compressive experiments were conducted on selected samples at room temperature. Comparison with the initial powder demonstrated that the extrusion rate of 6 mm/sec and the extrusion die temperature of $T_g$ + (25-35 K) results in the best consolidation quality (near full density, near theoretical shear deformation of prior particles and strong in terparticle bonding). No significant crystallization peaks are observed in XRD measurements. The DSC measurements of these consolidates is not significantly different than that of initial powder. Microhardness indentations demonstrate shear localization patterns around indents without crack formation under a 1 kg load. A compressive strength of about 1.6 GPa is observed in the best consolidated samples, which is very close to what is observed in cast material. The fracture surfaces of these compression samples exhibit vein patterns typical of metallic glass fracture. Occasional interparticle debonding in some samples is observed. The results of the present study demonstrate that ECAE consolidation may be a viable method for the fabrication of bulk metallic glass.

**3:30 PM Break**

**3:45 PM Invited**
**Early Stages of Decomposition of Bulk Metallic Glasses**: *Michael K. Miller*[1]; [1]Oak Ridge National Laboratory, Metals & Ceram. Div., PO Box 2008, Oak Ridge, TN 37831-6136 USA

The transformation of bulk metallic glasses from the amorphous state to the fully crystalline state is of interest to evaluate the stability of the glasses. High resolution microstructural characterization of these microstructures provides important information concerning the decomposition processes. Atom probe tomography has been applied to several different bulk metallic glasses to evaluate the microstructural changes that occur between the as-cast state and after annealing in the vicinity of the glass transition temperature. The spatial coordinates and the elemental identities of the atoms in the alloy may be determined with near atomic resolution. The three-dimensional data collected can be analyzed to determine the local atomic configuration around each atom type. Research at the Oak Ridge National Laboratory SHaRE Collaborative Research Center was sponsored by the Division of Materials Sciences and Engineering, US Department of Energy, under contract DE-AC05-00OR22725 with UT-Battelle, LLC.

**4:05 PM Invited**
**Preparation and Properties of Carbon-Nanotube-Reinforced Zr-Based Bulk Metallic Glass Matrix Composites**: *Weihua Wang*[1]; Zan Bian[1]; [1]Chinese Academy of Science, Inst. of Physics, Beijing 100080 China

ZrCuNiAlTi bulk metallic glass composite containing carbon nanotubes (c-tubes) up to 10 vol.% were prepared successfully. The composite consists of c-tubes, ZrC phase and the glass matrix. The mechanical properties, Vickerís hardness and elastic moduli of the composite are markedly improved relative to the undoped bulk metallic glass (BMG). Measurement of acoustic attenuation shows that ultrasonic attenuation coefficient increase drastically after adding c-tubes into BMG, the relative changes in the longitudinal and transverse ultrasonic attenuation (_l and _t) are up to 900% and 536% for BMGC containing 4 vol. % c-tube addition. The results indicate that the composites have excellent acoustic wave absorption ability originating from the structural variation induced by adding c-tubes into the BMG. The excellent acoustic absorption ability may lead to application of BMGs in the field for shielding acoustic sound.

**4:25 PM**
**Structure Property Relations of Simulated Amorphous Ni/Zr Alloys**: *Frank J. Cherne*[1]; Michael I. Baskes[1]; Ricardo B. Schwarz[1]; Srivilliputhur G. Srinivasan[1]; [1]Los Alamos National Laboratory, MST-8, Struct. & Prop. Rel., PO Box 1663, MS G755, Los Alamos, NM 87545 USA

Using molecular dynamics and a modified embedded atom method potential developed by our group, we study the structural and elastic properties of amorphous nickel-zirconium alloys as a function of composition and temperature. Previous results indicate that these potentials describe the Ni/Zr system quite well. Liquid alloys were quenched with rates from 2.5 x $10^{11}$ to 5 x $10^{12}$ K/s. Using a common neighbor analysis algorithm, we determine the structural units within the liquids and the amorphous solids near the glass transition ($T_g$). We are interested in $X_{Zr}$ between 12% and 75% where experimentally amorphous materials have been formed. Within this composition range, we observe amorphous material formation. We examine the effects of composition and cooling rates on the local neighbor coordination in the quenched samples.

**4:40 PM**

**In-Situ Study of Decomposition Kinetics in Bulk Metallic Glass $Zr_{52.5}Cu_{17.9}Ni1_{4.6}Al_{10}Ti_5$ by Simultaneous Synchrotron X-Ray Diffraction and Small Angle Scattering**: *Xun-Li Wang*[1]; J. D. Almer[2]; Y. D. Wang[1]; J. K. Zhao[1]; D. R. Haeffner[2]; C. T. Liu[1]; [1]Oak Ridge National Laboratory, Spallation Neutron Source & Metals & Ceram. Div., PO Box 2008, Oak Ridge, TN 37831 USA; [2]Argonne National Laboratory, Adv. Photon Source, Argonne, IL 60439 USA

Controlled decomposition of bulk metallic glass precursors offers a promising way for synthesis of nanostructured materials in large quantities. The decomposition of bulk metallic glass involves a multi-stage phase separation of the amorphous and crystalline phases. Despite current research efforts, details of the decomposition kinetics remain sketchy. We report here a simultaneous diffraction and small angle scattering study using high-energy synchrotron X-ray. The diffraction experiment gives the kinetics of the phase transformations, while the small angle scattering experiment reveals the process of phase separation. Our experiment on $Zr_{52.5}Cu_{17.9}Ni1_{4.6}Al_{10}Ti_5$ at T=700 K shows that the crystallization and phase separation initiate simultaneously. The diffraction peak intensity (from the $Zr_2Ni$ phase) increases abruptly at the onset of the phase transformation and quickly saturates. The intensity of small angle scattering, on the other hand, saturates at a slower rate. Analysis of both sets of data suggests that the decomposition in $Zr_{52.5}Cu_{17.9}Ni1_{4.6}Al_{10}Ti_5$ begins with site-saturated nucleation of the crystalline phase, followed by slow growth of the nanosized crystalline precipitates and a redistribution of chemical composition in each phase to reach the thermodynamic equilibrium. Research sponsored by the Division of Materials Sciences and Engineering, Office of Basic Energy Sciences, US Department of Energy, under Contract DE-AC05-00OR22725 with UT-Battelle, LLC.

**4:55 PM**

**Low-Temperature Magnetization and Spin-Wave Excitations in Bulk Fe-Based Amorphous Glasses**: *Tong D. Shen*[1]; Ricardo B. Schwarz[1]; Joe D. Thompson[2]; [1]Los Alamos National Laboratory, MST-8, MS G755, Los Alamos, NM 87545 USA; [2]Los Alamos National Laboratory, MST-10, MS K764, Los Alamos, NM 87545 USA

Our flux-purified Fe-Cr-Mo-Ga-P-B-C bulk ferromagnetic glasses have significantly lower AC power losses than rapidly quenched Fe-based glassy ribbons. We have used a SQUID magnetometer to study the temperature dependence of the DC magnetization in bulk Fe-Ni-P-B and Fe-Cr-Mo-Ga-P-B-C glasses. The temperature dependence of the DC magnetization has been extensively studied for glassy ribbons, but not for the newer bulk ferromagnetic glasses. We conclude that: 1) Alloying elements such as Cr, Mo, and Ga decrease the magnetization and Curie temperatures; 2) The low-temperature magnetization-temperature relations for our Fe-based bulk glasses are well described by spin-wave theory; 3) Our bulk metallic glasses have stronger spin-wave stiffness constants than glassy ribbons, indicative of a wider exchange-interaction range. This further suggests that the bulk ferromagnetic glasses have stronger short-range order or are phase separated; 4) Structural relaxation achieved by annealing the bulk glasses below their glass-transition temperatures further enhances the exchange interaction.

**5:10 PM**

**Thermodynamic Prediction of Potential Multicomponent Alloys to Form Metallic Glasses**: *K.-C. Hsieh*[1]; D. Ling[2]; Y. Pan[3]; G.-X. Sun[3]; Y. Austin Chang[2]; [1]National Sun Yat-Sen University, Inst. of Matls. Sci. & Eng., Kaohsiung 80424 Taiwan; [2]University of Wisconsin, Dept. of Matls. Sci. & Eng., Madison, WI 53706 USA; [3]Southeast University, Dept. of Mechl. Eng., Nanjing, Jiangsu 210018 China

It is well recognized that the existence of a deep eutectic favors glass formation. One example is soda silicate glass that forms at a eutectic composition of binary Na2O-SiO2. Moreover, we have recently calculated the compositions of liquid alloys at the five-phase invariants of Cu-Ni-Ti-Zr using the CALPHAD methodology (Intermetallics, 2001, 9, p553). These calculated values agree with those measured for bulk metallic glass formation (JAP, 1995, 78, p6514). Based on this success we have been calculating liquid alloy compositions initially for a number of quaternaries such as Al-Cr-Ni-Ti using computer software PANDAT. These calculated values are being used as an intelligent guide to rapidly develop metallic glasses experimentally. In this talk, we will present our preliminary results.

**5:25 PM**

**Preparation and Thermal Stability of Mechanically Alloyed Ni-Zr-Ti-Y Amorphous Powders**: *Pee-Yew Lee*[1]; [1]National Taiwan Ocean University, Matls. Eng., 2, Pei-Ning Rd., Keelung 202 Taiwan

Exploring amorphous alloys with a large supercooled liquid region before crystallization is of great importance because the appearance of the large supercooled liquid region is expected to cause the production of a bulk amorphous alloy. The large supercooled liquid region with a temperature interval above 60K had been observed in amorphous Zr-, La, and Mg-based alloys. However, a survey of the available literature indicates that little work has been performed on the formation of Ni-based amorphous alloy with large supercooled liquid region. Ni is a cheaper element as compared with Zr-, and Ti-based amorphous alloys and is expected to have better mechanical properties than that of Zr-based amorphous alloys. In this study, we have investigated the possibility of preparing amorphous Ni-Zr-Ti-Y powders by mechanical alloying of crystalline elemental powder mixtures using a shaker ball mill. The glass-forming ability and thermal stability of mechanically alloyed Ni-Zr-Ti-Y powders were determined by using X-ray diffraction and differential scanning calorimetry (DSC). The results indicated that several amorphous alloy samples were found to exhibit a wide supercooled liquid region before crystallization. This is believed to be the first evidence for the appearance of a supercooled liquid region for mechanically alloyed Ni-Zr-Ti-Y amorphous powders. The finding of the new Ni-Zr-Ti-Y amorphous powders with wide supercooled liquid region is promising the future development of a new Ni-based bulk amorphous alloy through powder metallurgy route.

## International Symposium on Structures and Properties of Nanocrystalline Materials: Magnetic and Other Functional Properties

*Sponsored by:* Structural Materials Division, Electronic, Magnetic & Photonic Materials Division, SMD-Mechanical Behavior of Materials-(Jt. ASM-MSCTS), Jt. EMPMD/SMD-Chemistry & Physics of Materials Committee

*Program Organizers:* Sung H. Whang, Polytechnic University, Department of Mechanical Engineering, Brooklyn, NY 11201 USA; Robert D. Shull, NIST, Magnetic Materials, Gaithersburg, MD 20899-8552 USA

Tuesday PM — Room: 14B
March 4, 2003 — Location: San Diego Convention Center

*Session Chairs:* R. Ramesh, University of Maryland, Dept. of Matls. Sci., College Park, MD 20742 USA; Robert D. Shull, NIST, Magnetic Matls., Gaitherburg, MD 20899-8552 USA

**2:00 PM**

**Surface and Interface Magnetism Studied by Depth Selective M^ssbauer Spectroscopy**: *Branko Stahl*[1]; [1]Technische Universitat Darmstadt, Matls. & Geo Scis., Thin Films, Petersenstrasse 23, Darmstadt D-64287 Germany

In nanostructured bulk materials the grain boundaries play a crucial role. The experimental characterization of such materials is complicated by the small size of the grains and their complex interaction with neighboring ones. It can be useful for an understanding of the properties of nanostructured materials to choose a simplified geometrical structure that fits to the spatial and time resolution of the experimental method. We have studied the magnetic properties of surfaces of insulating antiferromagnetic single crystals, thin films and nanoparticles to distinguish between pure surface and finite size effects. In two related examples the antiferromagnetic to paramagnetic phase transition could be followed as a function of depth (0-300 nm) and temperature by a depth selective M^ssbauer technique. In the first case (FeBO3), a non-expected magnetic wetting phenomenon is observed. The dynamics of the magnetic moments is changed with respect to the bulk material. In the second case ((Fe,Ga)BO3), the exchange of 24% of the Fe by Ga leads to the expected ordinary phase transition with a gradual decrease of the order parameter towards the surface. These findings support the concept that already the presence of a pure surface is able to alter the magnetic ordering in a certain depth region. The experimental results have parallels in structural phase transitions at surfaces and grain boundaries. Currently experiments are undertaken to study the observed magnetic behavior also in systems with reduced spatial dimensions, i.e. in thin films and nanoparticles. The peculiar properties of nanosized systems is also demonstrated in the case of a metal ferromagnet. 4 nm particles of FePt were characterized by Rutherford backscattering spectroscopy, x-ray diffraction, transmission electron microscopy, x-ray photoelectron spectroscopy, M^ssbauer spectroscopy and magnetometry. The results shed light on the metallic properties of the particles core as well as the chemistry of the particles surface with the organic ligands. Due to the well defined size of the particle-ligand system 3-dimensional superlattices are formed.

**2:30 PM**

**Nano-Structured Alloys with Soft Magnetic Properties**: *Ricardo B. Schwarz*[1]; Tong D. Shen[1]; Thomas M. Lillo[2]; [1]Los Alamos National Laboratory, MST-8, MS G755, Los Alamos, NM 87545 USA; [2]INEEL, Matls. Div., PO Box 1625, MS 2218, Idaho Falls, ID 83415-2218 USA

Soft ferromagnetism is obtained in both amorphous and nanocrystalline alloys. Amorphous alloys, however, have relatively low saturation magnetization (< 1.2 Tesla) and one dimension less than about 5 mm. The consolidation of alloy powders with nanocrystalline grains may enable the synthesis of bulk materials having both low coercivity and high saturation magnetization. Single-phase Fe-Cu alloy powder with nanosized grains was prepared by mechanical alloying. Annealing the powder at 450K reduces the residual strains without causing significant grain growth. Equal-channel angular extrusion was used to consolidate the powder into rods. The magnetic properties of the consolidated material were measured on small transformers made on toroid-shaped specimens cut from the rods. These toroids had saturation magnetization of 1.5 Tesla and coercivity of 3 Oe. Annealing treatments were used to reduce the internal stresses introduced by the consolidation process and to decrease the coercivity.

**3:00 PM**

**Nanoscaled Magnetostrictive Thin Films for Sensor Applications**: *Eckhard Quandt*[1]; Alfred Ludwig[1]; Michael Frommberger[1]; Christel Zanke[1]; Markus Loehndorf[1]; [1]Caesar, Smart Matls., Friedensplatz 16, Bonn D-53111 Germany

Magnetostrictive materials are attractive transducers for applications in MEMS and nanotechnology since they allow simple designs and processing routes which can be scaled down over a wide range of magnitudes without loosing their principle feasibility. While actuators are based on the direct magnetostrictive effect or the □E effect, sensors for mechanical quantities can be realized by combining the inverse magnetostriction with other effects like magnetoimpedance, magnetoresistance or inductivity. In order to meet certain requirements like e.g. the cut-off frequency the thin film materials themselves have to be controlled in terms of their microstructure on a nm-scale. The presentation will discuss the properties of different nanoscaled magnetostrictive materials in view of their possible applications in areas like automotive industry, information technology and biotechnology. Financial support provided by the German Ministry of Education and Research (BMBF 03N3089 and 13N7943) and the Office of Naval Research (N00014-02-1-0231) is gratefully acknowledged.

**3:30 PM**

**Novel Nanostructured Hydride Composites: Hydrogen Storage Materials for Mobile Applications**: *R. Bormann*[1]; T. Klassen[1]; W. Oelerich[1]; E. Martinez[1]; [1]GKSS Research Center, Inst. for Matls. Rsrch., Geesthacht D-21502 Germany

A breakthrough in hydrogen storage technology was achieved by preparing nanostructured hydride composites using novel catalysts1. These new composite materials advanced ab- and desorption kinetics, thus qualifying e.g. lightweight Mg-based hydrides for storage application. In this talk, an overview on the sorption behaviour of nanocrystalline Mg and Mg-based composites will be presented, demonstrating their potential as a high-temperature hydride (T=250-300∞C) with a storage capacity up to about 7 wt.% hydrogen. Current research is focussed on alanate-based composites for application temperatures between 100-200∞C. Recent results on the thermodynamics and the sorption behaviour will be presented.

**4:00 PM**

**Ionic Conductivity in Nanometer-Scale Heteroepitaxial YSZ Films**: *Christopher M. Rouleau*[1]; Igor P. Kosacki[2]; Paul F. Becher[2]; Douglas H. Lowndes[1]; [1]Oak Ridge National Laboratory, Solid State Div., PO Box 2008, MS 6056, Oak Ridge, TN 37831 USA; [2]Oak Ridge National Laboratory, Metals & Ceram. Div., PO Box 2008, MS 6068, Oak Ridge, TN 37831 USA

Enhanced ionic transport can be achieved in technical oxides, such as zirconia, by generating oxygen vacancies via acceptor doping or by increasing the ionic mobility by accentuating fast diffusion pathways. Recent studies have shown that these methods are effective due to grain boundary and interfacial effects found in materials with nanometer-scale microstructures. These effects dominate in nanocrystalline materials, for example, when the grain size is less than 100nm. Here we examine the influence of film thickness on the ionic conductivity of 10mol% yttria stabilized zirconia thin-films (YSZ) deposited onto MgO by pulsed laser ablation. In this geometry, the fraction of conducting pathways at the surface and heterointerface, versus that within the bulk, varies with film thickness and leads to an overall conductivity having contributions from each. The conductivity was measured in-plane as a function of film thickness and temperature using 2-point impedance spectroscopy and it was found that films having thicknesses >50nm mimicked bulk YSZ while those below 50nm had remarkably higher conductivities. Using a percolation model, it was determined that the surface/heterointerface-related conductivity was two orders of magnitude greater than that of the bulk.

**4:30 PM**

**Nanocrystalline FeCo Powders Produced by Mechanical Milling**: *I. Baker*[1]; M. Robson[2]; Ryan G. Quiller[3]; [1]Dartmouth College, Thayer Sch. of Eng., 8000 Cummings Hall, Hanover, NH 03755 USA; [2]The Cooper Union for the Advancement of Science and Art, Cooper Sq., New York, NY 10003-7120 USA; [3]Rensselaer Polytechnic Institute, Dept. of Math., 110 8th St., Troy, NY 12180 USA

Fine powders of Fe and Co were mechanically-milled for 60 hours using stainless steel balls in a Svegari attritor operated under an argon atmosphere. The effects of various elemental additions, including B, C Cu, Zr and Ni, on the microstructure of approximately stoichiometric Fe:Co powders were studied. The morphologies and sizes of the powders were examined using a scanning electron microscope. The grain sizes and phases present before and after annealing the milled powders at 873 K were examined using X-ray diffractometry. Phase transformations in the milled powders were examined using constant heating in a differential scanning calorimeter. The resulting magnetic properties were measured using a vibrating sample magnetometer. Research sponsored by NSF grants DMR-9820408, DMR-9973977 and DMR-0139085.

**4:50 PM**

**Sol-Gel Derived Nanocrystalline Tin Oxide Based Hydrogen Gas Sensor**: *Satyajit Vishnu Shukla*[1]; Sudipta Seal[1]; Suresh Kuiry[1]; Swanand Dilip Patil[1]; Lawrence Ludwig[2]; Clyde Parish[2]; [1]University of Central Florida, Dept. of Mechl. Matls. Aeros. Eng., 4000 Central Florida Blvd., Eng # 381, Orlando, FL 32826 USA; [2]Kennedy Space Center (NASA) and University of Central Florida, Orlando, FL 32826 USA

Nanocrystalline tin oxide (SnO2) based hydrogen (H2) gas sensor, in the form of thin film, operating at room temperature is synthesized using sol-gel technique utilizing alkoxide and non-alkoxide precursors. The effect of sol-gel synthesis parameters such as solution as well as polymer concentrations and firing temperature on various sensing parameters such as sensitivity, response and recovery time are systematically investigated. The use of hydroxypropyl cellulose (HPC) polymer is shown to control the nanocrystallite size and the amount of porosity within the thin film. The effects of surface and bulk modifications of SnO2 obtained via sputtering and doping techniques respectively are demonstrated as useful techniques to achieve maximum H2 gas sensitivity at room temperature. The sensor is characterized using various analytical techniques such as XPS, SEM, and HRTEM to optimize its performance.

**5:10 PM**

**Magnetic Nanomaterials for Defense and Biotechnology Applications**: *R. V. Ramanujan*[1]; H. F. Li[1]; S. W. Du[1]; [1]Nanyang Technological University, Sch. of Matls. Eng., Nanyang Ave. 639798 Singapore

Novel soft magnetic nanomaterials have been shown to exhibit excellent properties, ongoing work on developing such iron and cobalt based alloys will be presented. The Herzer model has shown that in suitable alloy systems, nanosized precipitates embedded in an amorphous matrix can yield superior magnetic properties. Such nanocrystalline magnetic materials can be produced crystallization, through heat treatment, of amorphous precursors, however the optimum alloy composition and heat treatment conditions have to be experimentally determined. Therefore, melt spun iron based alloys with the composition (in wt. %) Fe40-Ni38-B18-Mo4 and Fe67-Ni18-B14-Si1 as well as cobalt based alloys of composition Co69-Si15 -B14-Fe4-Ni1 and Co81-Si7-Mo4-B3-Ni1 have been studied by a variety of experimental techniques such as TEM, EDX, XRD, VSM, resistivity and DSC. Heat treatment of these alloys showed a variety of interesting crystallization reactions. The DSC results provided the primary and secondary crystallization temperatures and the activation energy of crystallization were extracted by the Kissinger analysis. Resistivity measurements identified the time for crystallization while VSM provided the magnetic properties as a function of heat treatment conditions. TEM and EDX were used to identify the morphology, distribution, structure and composition of the crystalline phase. Based on the above results, selected alloys, heat treated at suitable temperatures and times, were evaluated for use in high temperature motors used in defense and for drug delivery in biotechnology applications.

**5:30 PM**

**Magnetic Structure and Hysteresis in Hard Magnetic Nanocrystalline Film: A Computer Simulation Study**: *Yongmei M. Jin*[1]; Yu U. Wang[1]; Armen G. Khachaturyan[1]; Andrei Kazaryan[2]; Yunzhi Wang[2]; David E. Laughlin[3]; [1]Rutgers University, Ceram. & Matls. Eng., 607 Taylor Rd., Piscataway, NJ 08854 USA; [2]The Ohio State University, Matls. Sci. & Eng., 2041 College Rd., Columbus, OH 43210 USA; [3]Carnegie Mellon University, Matls. Sci. & Eng., Pittsburgh, PA 15213 USA

Three-dimensional micromagnetic simulations are used to study the effect of textures on the magnetic properties of uniaxial nanocrystalline films of hard magnetic materials with arbitrary grain shapes and size distributions. The correlation lengths of these hard magnetic materials, domain wall width and ferromagnetic exchange length, are assumed to be smaller than the typical grain size. The Landau-Lifshitz equations of the magnetization dynamics are employed to describe the distribution of magnetization in ferromagnetic domains, domain evolution during magnetization switching, and the hysteresis curve. The equations are solved numerically in reciprocal space using the Fast Fourier Transform technique. Simulations are performed for films of different grain textures. The results show that the magnetic coupling between grains in thin film significantly affects the morphology of magnetic domains and their response to the applied magnetic field. The greater the deviation of grain uniaxial directions from the film normal, the smaller the coercivity and the remanence magnetization. It is also shown that the remanence magnetization and coercivity respond differently to the variations in film texture and that the magnetic reversal process is a collective process involving groups of grains. In particular, it is found that the grain texture has a more complicated effect on the coercivity than on the remanence magnetization and on the character of topological changes during magnetization reversal process.

## Lead-Free Solders and Processing Issues Relevant to Microelectronics Packaging: Microstructural Characterization and Evolution

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

*Program Organizers:* J. P. Lucas, Michigan State University, Chemical Engineering and Materials Science, East Lansing, MI 48824 USA; Srini Chada, Motorola, Department APTC, Plantation, FL 33322 USA; Sung K. Kang, IBM, T. J. Watson Research Center, Yorktown Heights, NY 10598 USA; C. Robert Kao, National Central University, Department of Chemical and Materials Engineering, Chungli City 32054 Taiwan; Kwang-Lung Lin, National Cheng Kung University, Department of Materials Science and Engineering, Tainan 70101 Taiwan; Jud Ready, MicroCoating Technologies, Atlanta, GA 30341 USA; Jin Yu, KAIST, Center for Electronic Packaging Materials 305-701 Korea

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*Session Chairs:* Sung K. Kang, IBM, T. J. Watson Rsrch. Ctr., Yorktown Heights, NY 10598 USA; C. Robert Kao, National Central University, Dept. of Cheml. Eng., Chungli City 32054 Taiwan

**2:00 PM Invited**

**Damage Accumulation and Failure of Sn-Based Electronic Solder Joints Under Thermomechanical Fatigue**: J. G. Lee[1]; *K. N. Subramanian*[1]; T. R. Bieler[1]; [1]Michigan State University, Dept. Cheml. Eng. & Matls. Sci., E. Lansing, MI 48824-1226 USA

The residual mechanical properties of thermomechanically fatigued (TMF) Sn-based solder joints initially deteriorate rapidly and tend to stabilize after the first few hundred cycles, in spite of additional surface damage accumulation. Such findings suggest that crack growth, rather than crack nucleation, is the controlling factor in TMF failures. Since several processes, such as creep/stress relaxation, aging, reversed shear, Sn-anisotropy, etc., contribute toward TMF failure, solder joints possessing similar geometry were subjected to these processes. These solder joints were examined by laser confocal microscopy, SEM, Orientation Imaging, and continuous documentation of microscopic damage accumulation. The relative importance of each of these contributing factors to TMF will be discussed in order to form a comprehensive picture consistent with the observed damage accumulation and mechanical behavior. Acknowledgement: Project funded by National Science Foundation under grant No. NSF-DMR-0081796.

**2:25 PM**

**Evolution of Microstructure and Damage in Tin-Lead Solder Under Fast Cyclic Loading**: *Yu-Lin Shen*[1]; Koel C.R. Abell[1]; Stephen E. Garrett[1]; [1]University of New Mexico, Dept. of Mechl. Eng., Albuquerque, NM 87131 USA

Accelerated testing of thermomechanical fatigue of solder joints typically employed a cyclic frequency on the order of 0.001 Hz or lower. At such a straining rate the mechanical and metallurgical (diffusion induced coarsening) effects both contribute to damage initiation and eventual failure. In the present study we focus on fast loading of eutectic tin-lead with frequencies of 1 Hz and higher. The primary purposes of conducting fast cyclic tests are (1) to keep the diffusional contribution at minimum so pure mechanical effects can be examined, and (2) to study solder reliability in microelectronics for space and military applications where severe stress environments such as mechanical shock and vibration prevail. As a baseline bulk specimens were first subject to relatively fast deformations of tension, compression and bending. Grain realignment and phase redistribution were observed and characterized by microscopy and microhardness indentation. A micromechanical model is proposed to elucidate the observed microstructural changes and progressive damage. The significance of damage evolution in the form of microscopic heterogeneity and mechanically induced phase coarsening caused by grain boundary sliding is illustrated. High-frequency twin-lap shear tests on solder joints were then performed. Phase coarsening and the associated fracture initiation were observed after only a short time, suggesting that long-term atomic diffusion is not a necessary factor in initiating coarsening and fatigue failure. Evidences of grain boundary sliding in the cyclically sheared small joints were also found. Progressive damage from microvoiding, coalescence of microvoids to form microcracks, to the development of a major crack during fast cyclic shearing will be presented and discussed.

**2:45 PM**

**Microstructure and Thermal Behavior of Sn-Zn-Ag Solders**: *Kwang-Lung Lin*[1]; Chia-Ling Shi[1]; [1]National Cheng Kung University, Matls. Sci. & Eng., 1 Ta-Hsuey Rd., Tainan 701 Taiwan

The microstructure and thermal behavior of Sn-Zn-Ag solder were investigated for 8.73~9%Zn and 0~3.0%Ag. SEM analysis shows Ag-Zn compound when the solder contains 0.1%Ag. XRD analysis results indicate that $Ag_5Zn_8$ and $AgZn_3$ become prominent when the Ag content is 0.3% and above. Meanwhile, the Zn-rich phase is refined and the Zn orientations gradually diminish upon increase in Ag content. The morphology of the Ag-Zn compound varies from nodular to dendrite structure when the Ag content increases. The growth of the Ag-Zn compounds is accompanied with diminishing of the eutectic structure of the Sn-9Zn solder. DSC investigation reveals that the solidus temperature of these solders exists at around 198°C. A single sharp exothermic peak was found for the solders with Ag content less than 0.5%. Liquidus temperatures were identified with the DSC analysis to vary from 206°C to 215°C when the Ag content ranges from 1.0% to 3.0%.

**3:05 PM**

**Interface Microstructure Between 42 Alloy and Sn-Based Lead-Free Solder**: *Chi Won Hwang*[1]; Jung Goo Lee[2]; Hirotaro Mori[2]; Katsuaki Suganuma[1]; [1]Osaka University, ISIR, Mihogaoka8-1, Ibaraki, Osaka 567-0047 Japan; [2]Osaka University, UHVEM, Mihogaoka 7-1, Ibaraki, Osaka 567-0047 Japan

42 alloy (Fe-42wt%Ni) has been widely used as one of the useful electrode materials in electronic devices. The interfacial characteristics between the Sn-base solder and 42 alloy, however, have not been fully understood yet. To examine interface microstructure, three types of lead-free solder, Sn, Sn-3.5Ag, and Sn-3Ag-0.5Cu, were used as lead-free solders. After joining, cross-sectioned samples against soldered layer were prepared and investigated by TEM, SEM, and EPMA. As an interfacial reaction layer between solder and 42 alloy, $FeSn_2$ phase was developed in a thickness of about 100 nm. Ni from 42 alloy dissolved in the molten solders and it formed $Ni_3Sn_4$ phase with Sn. Microstructure of interface was also evaluated in detail.

**3:25 PM**

**Characterization and Microstructure Evolution of Thermomechanically Fatigued Dual Single Shear Lap Sn-Ag Solder Using Orientation Imaging Microscopy**: *A. U. Telang*[1]; T. R. Bieler[1]; J. G. Lee[1]; K. N. Subramanian[1]; [1]Michigan State University, Dept. of Cheml. Eng. & Matls. Sci., E. Lansing, MI 48824-1226 USA

Single shear lap specimens having a solder joint area of 1 $mm^2$ and thickness of 80-160 μm on copper and nickel substrates were thermomechanically (TMF) cycled from -15 to 150°C in order to mimic solder joint deformation history of surface mount components. SEM studies reveal that shear bands, surface relief effects and other surface morphological features develop even after tens of TMF cycles. Orientation imaging (OIM) studies of various regions of specimens that underwent 0, 20, 100, 500, and 1000 TMF cycles were carried out to determine how the microstructure and crystallographic orientations evolve during TMF. These results were compared to those of unconstrained single shear lap specimens to ascertain the substantial role of reversed shear deformation and the anisotropy of Sn that lead to failure of the solder joints in surface mount components. Supported by National Science Foundation under grant NSF DMR-0081796.

**3:45 PM Break**

**3:55 PM Invited**
**A Strategy for Producing Adaptive Lead-Free Solder Joints Via Shape-Memory Alloy Reinforcement of Solder Alloys**: *Indranath Dutta*[1]; Bhaskar S. Majumdar[2]; Sunglak Choi[1]; William Wright[1]; [1]Naval Postgratuate School, Dept. of Mechl. Eng., 700 Dyer Rd., Code ME/DU, Monterey, CA 93943 USA; [2]New Mexico Tech, Dept. of Matls. Sci. & Eng., Socorro, NM 87801 USA

Microelectronic solder joints are typically exposed to aggressive thermo-mechanical cycling (TMC) conditions during service. During TMC, strain localization occurs near solder/bond pad interfaces, where large inelastic shear strains accumulate, eventually causing low-cycle fatigue failure of the joint. In this paper, a new methodology to mitigate the effects of strain localization within the joint are discussed, wherein the solder alloy is reinforced with Ni-Ti based shape memory alloy (SMA) whiskers with a martensite-to-austenite (MÆA) transformation temperature of 80-100∞C are used to reinforce a Sn-4.7%Ag-1%Cu solder. In this scheme, the SMA reinforcement undergoes MÆA transformation near the high temperature end of the TMC, placing the solder matrix next to the solder/bond pad interfaces in reverse shear, enabling strain redistribution and homogenization, and thereby enhancing joint life. The conceptual mechanics of this adaptive scheme will be presented, along with issues relating to the fabrication of SMA reinforced lead-free solders. Some experimental results delineating the role of SMA reinforcement on the overall joint behavior will also be presented. Supported by the Army Research Office. The assistance of Dr. Treliant Fang of Form Factor, Inc. is gratefully acknowledged.

**4:20 PM**
**Effect of Cooling Rate on the Microstructure of Ag-Cu-Sn**: Leonid Snugovsky[1]; Polina Snugovsky[2]; *Doug D. Perovic*[1]; John Rutter[1]; [1]University of Toronto, Dept. of Matls. Sci. & Eng., Wallberg Bldg., 184 College St., Toronto, Ontario M5S 3E4 Canada; [2]Celestica, Matls. Lab., STC, 844 Don Mills Rd., Toronto, Ontario M3C 1V7 Canada

Samples of four Pb-free compositions in the Ag-Cu-Sn system were cooled at various rates and examined metallographically to evaluate microstructural effects. For Ag and Cu contents less than that of the ternary eutectic composition, faster cooling rates produced greater amounts of primary tin dendrites with interdendritic eutectic containing as much as 15 vol.% of compound phases. For Ag and Cu contents greater than that of the ternary eutectic composition, smaller amounts of primary Sn dendrites and increasing amounts of ternary eutectic microstructure were observed. In some samples, binary Ag3Sn-Sn eutectic was also observed. It was found that the Sn phase contained up to 1 wt. % Ag in solution, in the absence of Cu. It is believed there occurs an effective kinetic shift in the eutectic point resulting from the greater undercooling required to drive freezing of the faceting compound phases at the same speed as the nonfaceting Sn phase.

**4:40 PM Invited**
**Microstructure Characterization in the Sn-Ag Solder Joints Between Stud Bumps and Metal Pads**: Mu-Seob Shin[1]; *Young-Ho Kim*[1]; Won-Chul Do[2]; Sun-Ho Ha[2]; [1]Hanyang University, Dept. of Matls. Eng., 17 Haengdang-dong, Seongdong-gu, Seoul 133-791 Korea; [2]Amkor Technology Korea, R&D Ctr., Seongsu-dong 2-ga, Seongdong-gu, Seoul 133-120 Korea

The microstructure of the flip chip solder joints fabricated using stud bumps and Pb-free solders were characterized as functions of reflow cycles and aging time. The Au or Cu stud bumps formed on Al pads in Si dies were aligned to corresponding metal pads in the substrates, which had been printed with Sn-3.5Ag pastes. The solder joints were made using reflow. In the solder joints fabricated using Au stud bumps, Au-Sn intermetallics spread over in the whole joints and the solder remained randomly as an island shape due to the fast dissolution of Au. The microstructure of the solder joints did not changed significantly even after multiple reflows. AuSn4 was the main phase after reflow, but AuSn4 and AuSn2 were converted to AuSn during aging. In the solder joints fabricated using Cu stud bumps, the Cu6Sn5 was formed only in the Cu interface and the solder was the main phase.

**5:00 PM**
**The Effects of Cooling Rate and Aging Temperature on Microstructure Evolution in Sn-Ag/Cu and Sn-Ag-Cu/Cu Joints**: *George Piotrowski*[1]; Jason J. Williams[1]; Nikhilesh Chawla[1]; [1]Arizona State University, Dept. of Cheml. & Matls. Eng., Tempe, AZ 85287-6006 USA

The morphology, thickness and evolution of the intermetallic compounds at the solder/metallization interface has a significant effect on the mechanical behavior of the overall solder joint. Thus, it is important to understand the roles that cooling rate and thermal aging have on the growth of the intermetallic compounds in the solder joints. Sn-3.5Ag and Sn-3.5Ag-0.7Cu solder/Cu ìsandwichî joints were reflowed and cooled in one of three different media (water, air, furnace) to obtain a controlled cooling rate. After cooling to room temperature, the solder joints were sectioned and aged at 100°C, 140°C, or 175°C for times ranging from 0h to 1000h. The thickness and morphology of the two intermetallic compounds present at the solder/metallization interface, $Cu_6Sn_5$ and $Cu_3Sn$, were examined. It will be shown that the cooling rate has a significant effect on the initial morphology and growth rate of the intermetallic compounds. It will also be shown that the rate of the total intermetallic growth, as well as $Cu_6Sn_5$ and $Cu_3Sn$, can be explained in terms of bulk and grain boundary diffusion. Research supported by the National Science Foundation (Program Manager: Dr. K.L. Murty, contract# DMR-0092530).

**5:20 PM**
**A Case Study of Sn Whisker Growth Phenomenon**: *Ker-Chang Hsieh*[1]; Shin-Jen Jack Wong[1]; Elton Yu[2]; C. C. Chen[2]; [1]National Sun Yat-Sen University, Inst. of Matls. & Eng., Kaohsiung 80424 Taiwan; [2]Philips Electronic Building Elements Industries (Taiwan), Ltd., Tech. Dev. Div., 10, Chin 5th Rd., N.E.P.Z., PO Box 35-48, Kaohsiung Taiwan

It is well understood that the root cause for whisker formation is the internal stress. The process factors such as plating current density, Sn layer thickness and intermetallic growth morphology could contribute to internal stress. Internal stress measured by XRD decreased as Sn whisker growth in a series of samples under low temperature aging storage. The local structures of Sn grain size, intermetallic and whisker root were examined by using focused ion beam (FIB). The preliminary results of this study are: (I) Plating current density will affect whisker formation. (II) Process flow especially thermal treatment step, will influence the whisker growth. (III) Moisture and electric current will affect whisker formation.

## Magnesium Technology 2003: Magnesium Casting Properties and Welding

*Sponsored by:* Light Metals Division, Materials Processing and Manufacturing Division, LMD-Magnesium Committee, International Magnesium Association, MPMD-Solidification Committee
*Program Organizers:* Howard I. Kaplan, US Magnesium LLC, Salt Lake City, UT 84116 USA; Menachem Bamberger, Technion, Israel Institute of Technology, Haifa 32000 Israel; John L. Mihelich, Metal Experts International, Winston, GA 30187 USA

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| Tuesday PM | Room: 2 |
| March 4, 2003 | Location: San Diego Convention Center |

*Session Chairs:* Alan Luo, General Motors, Matls. & Processes Lab., Warren, MI 48090-9055 USA; G. Cohen, Nuclear Research Center Negev, Beer Sheva 84190 Israel

**2:00 PM**
**Electrical and Thermal Conductivity Measurements on Commercial Magnesium Alloys**: *Sayavur I. Bakhtiyarov*[1]; Ruel A. Overfelt[1]; Sorin G. Teodorescu[1]; [1]Auburn University, Mechl. Eng., 202 Ross Hall, Auburn, AL 36849-5341 USA

The worldwide production of magnesium increased from 10 tonnes per annum in 1900 to 350,000 tonnes per annum during the 1990s. The need for magnesium alloys has increased rapidly because of their light weight (r=1.738 g◊cm-3 at 200C) and rigidity. Poor corrosion resistance of these alloys triggered the development of new corrosion resistant alloys with improved tensile strength and augmented stiffness. The amount of each alloying constituent (up to the solid solubility limit) strongly affects the physical and mechanical properties of magnesium. The distinctive physico-chemical properties of magnesium and its alloys require special techniques to accurately measure their thermophysical properties. A rotational inductive measurement technique has been modified and used to determine the electrical resistivity of magnesium alloy AE42 over a wide range of temperature (including the molten alloy). In addition, the thermal conductivity of the alloy was estimated from these data using the Wiedemann-Franz-Lorenz law.

**2:25 PM**

**Modelling of the Thermo-Physical and Physical Properties for Solidification of Mg-Alloys**: *Nigel Saunders*[1]; Xiuqing Li[2]; Alfred Peter Miodownik[1]; Jean-Philippe Schille[2]; [1]Thermotech, Ltd., Surrey Tech. Ctr., The Surrey Rsrch. Park, Guildford, Surrey GU2 7YG UK; [2]Sente Software, Ltd., Surrey Tech. Ctr., The Surrey Rsrch. Park, Guildford, Surrey GU2 7YG UK

The thermo-physical and physical properties of the liquid and solid phases are critical components in casting simulations. Such properties include the fraction solid transformed, enthalpy release, thermal conductivity, volume and density all as a function of temperature. Due to the difficulty in experimentally determining such properties at solidification temperatures, little information exists for multi-component alloys. As part of the development of a new computer programme for modelling of materials properties (JMatPro) extensive work has been carried out on the development of sound, physically based models for these properties. Extensive results will presented for Mg-based alloys.

**2:50 PM**

**Developments in Lost Foam Casting of Magnesium**: *Michael Marlatt*[1]; David Weiss[2]; John N. Hryn[3]; [1]wfv/Roeperwerk, Plymouth, WI USA; [2]Eck Industries, Inc., Manitowoc, WI 54221-0967 USA; [3]Argonne National Laboratory, Argonne, IL 60439-4815 USA

Preliminary work was conducted in the casting of magnesium using the lost foam casting process. The lost foam or expendable pattern casting (EPC) process is capable of making extremely complicated part shapes at acceptable soundness levels and with low manufacturing costs. Standard test shapes were used to determine the ability of the magnesium to fill the mold and to assess the types of defects encountered. This paper will briefly explain how this project evolved including the developmental strategies formed, the products selected, the casting trials performed, and the casting results.

**3:15 PM Break**

**3:30 PM Invited**

**Friction Stir Welding of Magnesium Alloys**: Richard Johnson[1]; *Philip L. Threadgill*[1]; [1]TWI, Ltd., Friction & Forge Processes Tech. Grp., Granta Park, Great Abington, Cambridge, Cambridgeshire CB1 6AL UK

Most magnesium alloys are relatively easy to weld, but avoiding some porosity in fusion welds is always difficult. This can be a particular problem in pressure die cast components, where small gas bubbles may be entrapped under very high pressure. This leads to a process instability during fusion welding, and poor quality welds. Solid state processes, in particular friction welding, can circumvent this problem, as no fusion occurs in normal circumstances. Furthermore, the parts being welded are also at a high pressure, limiting the ability of the trapped gas to expand. Of particular interest is the friction stir welding process, first developed at TWI in 1991, which has now been demonstrated as a powerful technique for welding magnesium alloys, in both cast and wrought forms. The process can also be used to join dissimilar magnesium alloys, and significant progress has also been made on joining aluminium alloys to magnesium alloys, a combination of particular interest to the automotive sector. This paper will summarise recent studies at TWI and elsewhere on friction welding of magnesium, with special emphasis on friction stir welding. The advantages and disadvantages of these approaches will be highlighted. The paper includes contributions on process data, microstructures and mechanical properties.

**3:55 PM Invited**

**Laser Welding of Magnesium Alloys**: *Kenneth Gordon Watkins*[1]; [1]University of Liverpool, Laser Grp., Dept. of Eng., Brownlow St., Liverpool L69 3GH UK

There is increasing current interest in the use of magnesium alloys in the automobile industry since the low density (and hence high specific strength) of these alloys may play a part in meeting directives aimed at reducing overall vehicle mass with subsequent reduction in the emission of greenhouse gases such as carbon dioxide. However, if the usefulness of these alloys is to be realised in applications of this type, successful joining methods are required. In the achievement of weight reduction based on the use of steel and aluminium alloys, it has been found that a tailored blank strategy based on laser welding has been very successful. This points to the necessity of increasing effort in the adaptation of laser beam welding techniques for the case of magnesium alloys. This paper reviews the joining of magnesium alloys by laser welding. It considers the influence of laser beam process parameters (laser power, welding speed, assist gas type and flow rate) on the weldability of these alloys, concentrating on factors such as elimination of porosity and the achievement of weld ductility and strength. Where appropriate, these factors are related to the metallurgy of the alloys concerned. The joining by laser welding of magnesium alloys to dissimilar alloys (particularly aluminium alloys) is also considered.

**4:20 PM**

**Welding and Weldability of AZ31B by Gas Tungsten Arc and Laser Beam Welding Processes**: *Sri Lathabai*[1]; Ken Barton[1]; Damien Harris[1]; Peter Lloyd[1]; Alasdair McLean[1]; [1]CSIRO, Mfg. & Infrastruct. Tech., PO Box 4, Woodville, S. Australia 5086 Australia

Welding will play an important role in the fabrication of modular lightweight structures based on magnesium alloy die castings, extrusion profiles and wrought products. Minimisation of rejection rates during fabrication requires that satisfactory weldability be established for a particular combination of materials and welding procedures. In this paper, we present the results of a study to quantify the weldability of wrought alloy AZ31B by gas tungsten arc (GTA) and laser beam (LB) welding processes. The susceptibility to weld metal solidification cracking was evaluated using the Varestraint and Circular Patch weldability tests. Operating windows of welding parameters for crack-free and porosity-free GTA and LB welding were identified, based on which welding procedures were developed for sheet and plate AZ31B. The microstructure and mechanical properties of welded test plates were assessed, leading to a better understanding of microstructural development and structure-property relationships in GTA and LB weldments in AZ31B.

**4:45 PM**

**Application of Welding Technologies for Joining of Mg Alloys: Microstructure and Mechanical Properties**: *Adin Stern*[1]; Abraham Munitz[2]; Gabrial Kohn[3]; [1]Ben Gurion University, Dept. of Matls. Eng., Beer-Sheva 84105 Israel; [2]Nuclear Research Center Negev, PO Box 9001, Beer Sheva 84190 Israel; [3]Rotem Industries, Rotem Industl. Park, PO Box 9046, Beer-Sheva 84190 Israel

Five welding technologies were investigated as a solution to the challenges of joining Mg alloys: Gas Tungsten Arc Welding, Electron Beam Welding, Magnetic Pulse Welds, Laser Assisted Friction Stir Welding and Resistance Spot Welding. The main influencing parameters have been analyzed using the joint strength and microstructure to evaluate the welding processes. The advantages and difficulties for each technique are described and discussed. The microstructural changes that occurred during welding were examined by optical microscopy and under the scanning electron microscope. Backscattered electron imaging giving pronounced compositional contrast was used, in combination with energy dispersive and wavelength dispersive spectroscopy microanalysis. Mechanical properties were determined by standard tensile tests on small-scale specimens and microhardness. The experimental results obtained in this study show that defect free welds could be obtained in magnesium alloys using the aforementioned welding techniques. These techniques hold good promises for industrial applications where reliable high quality joining methods are required. The present paper describes a part of a broader research program aimed at gaining a better understanding of the relationship between microstructure, properties and the welding technique, in Mg alloys welded joints.

## Magnesium Solidification, Casting and Welding –Jt. Session with Magnesium Technology 2003: Magnesium Casting and Solidification and Simulations

*Sponsored by:* Light Metals Division, Materials Processing and Manufacturing Division, LMD-Magnesium Committee, International Magnesium Association, MPMD-Solidification Committee
*Program Organizers:* Howard I. Kaplan, US Magnesium LLC, Salt Lake City, UT 84116 USA; Menachem Bamberger, Technion, Israel Institute of Technology, Haifa 32000 Israel; John L. Mihelich, Metal Experts International, Winston, GA 30187 USA

Tuesday PM — Room: 2
March 4, 2003 — Location: San Diego Convention Center

*Session Chairs:* Gerald S. Cole, Consultant, USA; David Henry StJohn, University of Queensland, CAST Div. of Matls. Eng., Brisbane, QLD 4072 Australia

See Tuesday AM Magnesium Technology 2003: Magnesium Casting and Solidification and Simulations symposium for abstracts.

## Materials Lifetime Science and Engineering - II

*Sponsored by:* Structural Materials Division, ASM International: Materials Science Critical Technology Sector, SMD-Mechanical Behavior of Materials-(Jt. ASM-MSCTS)
*Program Organizers:* Peter K. Liaw, University of Tennessee, Department of Materials Science and Engineering, Knoxville, TN 37996-2200 USA; Raymond A. Buchanan, University of Tennessee, Department of Materials Science and Engineering, Knoxville, TN 37996-2200 USA; D. Gary Harlow, Lehigh University, Mechanical Engineering and Mechanics, Bethlehem, PA 18015-3085 USA; Dwaine L. Klarstrom, Haynes International, Inc., Kokomo, IN 46904-9013 USA; Peter F. Tortorelli, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6156 USA; Robert P. Wei, Lehigh University, Mechanical Engineering and Mechanics, Bethlehem, PA 18015 USA

Tuesday PM — Room: 18
March 4, 2003 — Location: San Diego Convention Center

*Session Chairs:* Raymond A. Buchanan, University of Tennessee, Dept. of Matls. Sci. & Eng., Knoxville, TN 37996-2200 USA; Robert P. Wei, Lehigh University, Mechl. Eng. & Mech., Bethlehem, PA 18015 USA

**2:00 PM Invited**
**Adhesion and Reliability in Thin-Film Microelectronic Device Structures**: *Reinhold H. Dauskardt*[1]; [1]Stanford University, Dept. of Matls. Sci. & Eng., Stanford, CA 94305-2205 USA

The mechanical behavior and resistance to delamination profoundly influences the mechanical integrity of a wide range of thin-film device structures, particularly during chemical mechanical planarization (CMP) operations where fragile low-k brittle dielectrics are exposed to aqueous environments and additional mechanical loads. Such behavior is considered in a range of representative thin-film structures containing glass, polymer and metal layers frequently encountered in interconnect structures. Three classes of low-k dielectrics are considered: modified silica containing organic, inorganic/organic polymer hybrid, and organics involving aromatic hydrocarbon polymers which are shown to behave in a ductile manner. Interface fracture studies are described to characterize both critical adhesion values and subcritical debonding behavior under selected loading and environmental conditions typically encountered during CMP. Multi-scale models are developed to explain the effect of a range of salient interface proper ties on delamination and fracture behavior. These include interface morphology and chemistry, ductile Cu or dielectric layer thickness, elastic properties and thickness of the barrier layer, environmental species in CMP environments, and loading mode. Finally, the effect of more complex patterned thin-film structures are examined.

**2:30 PM Invited**
**Fracture, Fatigue and Structural Reliability of Bulk Metallic Glass Alloys: Hydrogen and Environmental Effects**: *Reinhold H. Dauskardt*[1]; [1]Stanford University, Dept. of Matls. Sci. & Eng., Stanford, CA 94305-2205 USA

The recent development of bulk metallic glass alloys offers the potential for a versatile new class of structural metallic materials with a range of superior mechanical and corrosion resistance properties. Availability of these materials in bulk form has also greatly facilitated the investigation of fundamental deformation, fracture and fatigue behavior compared to previous studies that were limited to thin metallic ribbons. This presentation will review the underlying deformation and fracture behavior in Zr-based bulk metallic glasses and their environmental sensitivity. Specifically, hydrogen and moisture are well-known embrittling species in a wide range of crystalline metals and their effects on the underlying kinetic flow processes and resulting fracture and fatigue behavior will be examined. Microstructure and thermal behavior of the metallic glass were examined using positron annihilation, high-resolution electron microscopy, X-ray diffraction, X-ray photoelectron spectroscopy and differential scanning calorimetry. The microstructural origin of selected environmental interactions in the amorphous microstructure will be identified. It will be demonstrated that hydrogen retards the fundamental molecular rearrangement process responsible for plastic flow in the amorphous metals. The sluggish molecular rearrangement process is believed to be responsible for increased flow stress and degraded toughness and fatigue behavior. The implications for reliability and structural integrity of bulk metallic glasses will be discussed.

**3:00 PM**
**Determining Worst-Case Fatigue Thresholds for Grain Bridging Ceramics**: *Jamie J. Kruzic*[1]; Rowland M. Cannon[1]; Robert O. Ritchie[1]; [1]Lawrence Berkeley National Laboratory, Matls. Scis. Div., 1 Cyclotron Rd., MS 62-203, Berkeley, CA 94720 USA

While many ceramics achieve increased toughness via grain bridging, they also suffer from cyclic fatigue failure due to degradation of the bridging zone and additionally should be susceptible to crack size effects when crack sizes become smaller than the bridging zone length. In order to investigate such crack size effects, a coarse grained (~18 micron) alumina was chosen as a model material. Crack-growth properties for both long (> 2 mm) and short (< 2 mm) cracks emanating from notches were investigated, with observed short crack growth rates exceeding those for corresponding long cracks at the same applied stress intensity range. Such results are rationalized by considering the reduced bridging zone for short relative to long fatigue cracks; indeed, after quantifying the effects of grain bridging and comparing the results in terms of an effective, bridging removed, stress intensity, a worst-case fatigue threshold is determined below which neither long nor short cracks appear to propagate. Since for structural applications crack sizes must remain small in ceramics components due to their inherent low toughness, such methodologies for predicting worst-case fatigue thresholds will be paramount for enabling fatigue lifetime predictions in grain bridging ceramics.

**3:20 PM**
**Localized Deformation Around Nanoindentations and the Effects of Hydrogen on Dislocation Cross-Slip**: *Kevin Andrew Nibur*[1]; [1]Washington State University, MSE, Pullman, WA 99164 USA

The ability to understand mechanical deformation on the nanometer to micrometer scale is important for developing accurate dislocation models. Atomic force microscopy (AFM) and orientation imaging microscopy (OIM) have been used to study dislocation cross-slip behavior around nanoindentations. Slip steps occurring in the pile-up region around an indentation have been characterized to determine the active slip systems resulting in each step. The frequency and magnitude of each step can be determined. These experimental results can be useful for dislocation dynamics models, since indentations can be selectively placed to either include or exclude interactions with grain boundaries, particles or other defects. This technique has been used to study hydrogen embrittlement in FCC and BCC materials to study the effect of hydrogen on dislocation cross-slip. Results indicate that hydrogen does not greatly affect the frequency of cross-slip, but does decrease the number of dislocations in a given slip step.

**3:40 PM Invited**
**Rotating-Beam Fatigue Properties and Effect of Additional Ni Element in Bulk Amorphous Zr50Cu40Al10 Alloys**: *Yoshihiko Yokoyama*[1]; Kenzo Fukaura[1]; Akihisa Inoue[2]; [1]Himeji Institute of Technology, Matls. Sci. & Eng., Shosha 2167, Himeji, Hyogo Pref. 671-2201 Japan; [2]Tohoku University, Inst. for Matls. Rsrch., Katahira 2-1-1, Aoba, Sendai, Miyagi Pref. 980-8577 Japan

In order to evaluate the effect of Ni element on fatigue strength, W^hler curves of Zr50Cu40Al10 and Zr50Cu30Ni10Al10 bulk glassy alloys were examined with rotating-beam fatigue test. We also observed fatigue feature surfaces of Zr50Cu40Al10 and Zr50Cu30Ni10Al10 bulk glassy alloys to estimate the effect of adding Ni element, which can improve the oxygen embrittlement in Zr-based bulk amorphous alloy. As the result, fatigue limit is increased from 250 MPa to 500 MPa by adding 10 at% Ni instead of Cu. Furthermore, by adding Ni element, fatigue-fractured region is limited inside of semi-circle region on the fractured surface. Besides, Zr50Cu40Al10 bulk glassy alloy shows wide fatigue-fractured region with striation like mark up to 90% under the low applied stress (close to fatigue limit) condition. Consequently, the prevent oxidization effect of Ni element is promotes fatigue limit in Zr50Cu40Al10 bulk glassy alloys.

**4:10 PM Invited**
**Mechanisms for Fatigue Crack Initiation and Early Propagation**: *Tongguang Zhai*[1]; [1]University of Kentucky, Dept. of Cheml. & Matls. Eng., 177 Anderson Hall, Lexington, KY USA

In this paper, a model for fatigue crack initiation has been proposed, based on the experimental results that there is always a net irreversible slip in one direction of the active slip in a metallic material. Such irreversible slip leads to a local stress which gradually breaks the material in the surface with the aid of environmental effects. The model appears to be able to explain the observed fatigue phenomena in Al, Cu, Cu-Al alloy and Mg single crystals. The paper has also discussed a crystallographic model for short crack growth across grain boundaries in a metallic material, especially those with strong tendency for planar slip. The main factor that controls the growth behavior of a short crack is the twist angle of crack deflection at the grain boundary plane. The short crack always chooses the path that forms the minimum twist angle in a new grain with the crack plane in the previous grain. These proposed models for crack initiation and early propagation could lead to more precise life prediction of a metallic material.

**4:40 PM Invited**
**Analysis of Plastic Deformation Behavior During Equal Channel Angular Pressing**: *Yong Liu*[1]; Zhihong Tang[1]; Baiyun Huang[1]; Kechao Zhou[1]; [1]Central South University, The State Key Lab. for Powder Metall., Changsha 410083 China

Equal channel angular pressing (ECAP) is a novel method for producing very high plastic strain, and, subsequently, ultrafine grains in materials, with no change in the billetís shape. However it is very important to understand the deformation behavior of the materials and their relationships with the friction condition and tooling configuration during the ECAP process before it can be exploited in the engineering field. In this study, the plastic deformation behavior of pure Al during the ECAP process with a die corner angle (120∫) was investigated using the commercial two-dimensional rigid-plastic finite element software (DEFORM2D). It has been found that the ECAP process was characterized by five steps based on the analysis of the calculated load-ram displacement curve (fast increase, slow increase, fast increase, steady and finally decreasing stages). The inhomogeneous strain distribution within the billets was analyzed by separating the billets into a front transient zone, an end transient zone, an outerless sheared zone, and the remaining shearing deformation zone, which is also proved by the experiment using the billets with scribed grids. The homogeneity of the strain distribution in the middle of billet is strongly dependent upon the material flow rate distribution and the stress state in the deformation zone. During the ECAP process, the stress state transits from the compressive stress to tensile stress in the inner part of the billets, while the stress state transits from the compressive stress, then tensile stress, and to compressive stress in the outer part of the billets, which, in part, attributes to forming inhomogeneous deformation. Due to the faster flow of the outer part compared with the inner part within the main deforming zone, the lesser shear zone in the outer part of the billets occurs. The inhomogeneity of deformation still occurs even under the condition of a free friction between the samples and the dies. However, if using a round die instead of a corner die, the material flow rate in the main deformation zone is nearly homogenous because of the inexistence of the tensile component in the outer part of the billets. Consequently, the homogeneity of deformation is greatly enhanced.

**5:10 PM**
**Evaluating the Induced Strain During Equal Channel Angular Processing**: *Grigoreta Mihaela Stoica*[1]; Peter K. Liaw[1]; [1]University of Tennessee, Matl. Sci. & Eng., 323 Dougherty Eng. Bldg., Knoxville, TN 37996-2200 USA

Grain refinement using Equal Channel Angular Processing (ECAP) has become well known in improving the mechanical properties of metals and composites. Any plasticity modeling of the microstructure changes during ECAP requires reliable macroscopic strain and strain rate data (and this is also consequential for comparing with other processes). The evaluation of the shear strain induced during one pass and/or multipass ECAP is still under debate, as well as the definition of the equivalent strain and strain rate. The present analysis is aimed at reconsidering the slip-line field (SLF) modeling in order to achieve a better description of the experimentally observed plastic deformation zone (PDZ) for ECAP severe plastic deformation. Strain and strain rate deduced using SLF theory are compared with finite element modeling (FEM) results for perfect-plastic and work-hardened materials. The SLF approach was used to describe the non-homogeneous deformation near the outer corner of the ECAP die by introducing the split of the shear plane into two cylindrical surfaces.

**5:30 PM**
**Molecular Processes in Creep and Durability of a Loaded Oriented Crystalline Polymer**: *Ulmas Gafurov*[1]; [1]Institute of Nuclear Physics, Tashkent 702132 Uzbekistan

Molecular models of chain slippage and rupture, interrelation of these molecular processes and durability for a loaded high-oriented amorphous-crystalline polymer is suggested. It is taken into account complex interaction between slippage and rupture of interconnecting polymer chains. According to the molecular model in polymer sample creep, chain rupture accumulation and polymer fracture the leading molecular process is mechanically stimulation of thermo-fluctuation slippage of interconnecting molecular chains. It is valid for flexible chain polymers at least. The activation energy value for the chain slippage process and consequently mechanical durability (fracture process) depend on intermolecular interaction and consequently on temperature and molecular chain flexibility.

## Materials Processing Fundamentals: Solidification and Forming Processes

*Sponsored by:* Extraction & Processing Division, Materials Processing & Manufacturing Division, Jt. MPMD/EPD-Process Modeling Analysis & Control Committee, EPD-Process Fundamentals Committee
*Program Organizers:* Adam C. Powell, Massachusetts Institute of Technology, Department of Materials Science and Engineering, Cambridge, MA 02139-4307 USA; Princewill N. Anyalebechi, Grand Valley State University, L. V. Eberhard Center, Grand Rapids, MI 49504-6495 USA

Tuesday PM — Room: 1A
March 4, 2003 — Location: San Diego Convention Center

*Session Chair:* Adam C. Powell, Massachusetts Institute of Technology, Dept. of Matls. Sci. & Eng., Cambridge, MA 02139-4307 USA

**2:30 PM**
**Directional Solidification of Commercial Brass**: Alicia Esther Ares[2]; Rubens Caram[3]; *Carlos Enrique Schvezov*[1]; [1]University of Misiones, Fac. of Scis., 1552 Azara St., Posadas, Misiones 3300 Argentina; [2]CONICET/University of Florida, Dept. of Matls. Sci. & Eng., 131 Rhines Hall, PO Box 116400, Gainesville, FL 32611-6400 USA; [3]State University of Campinas, Matls. Eng. Dept., Campinas, Sao Paulo CP 6122 Brasil

The columnar-to-equiaxed transition (CET) was observed in brass samples directionally solidified from the chill zone in different solidification conditions. The transition occurs when the gradient in the liquid ahead of the columnar dendrites reaches values between -2.23∞C/cm and 1.05∞C/cm and the growth velocities reach values between 0.13 cm/s and 0.34 cm/s. The microstructure obtained is analyzed taking into account the characteristics of the alloy and the temperature profiles at the solidification interface. The variation of the primary and secondary dendritic spacings along the length of the sample is analyzed and the values experimentally measured are compared with results predicted by different theoretical models.

**2:50 PM**
**The Effect of Solidification Parameters on Dendrite Spacing in Unidirectional Solidification**: Alicia Esther Ares[2]; Rubens Caram[3]; *Carlos Enrique Schvezov*[1]; [1]University of Misiones, Fac. of Sci., 1552 Azara St., Posadas, Misiones 3300 Argentina; [2]CONICET/University of Florida, Dept. of Matls. Sci. & Eng., 131 Rhines Hall, PO Box 116400, Gainesville, FL 32611-6400 USA; [3]State University of Campinas, Matls. Eng. Dept., Campinas, Sao Paulo CP 6122 Brasil

Experiments were carried out in which the conditions of dendritic growth are known, as well as the velocity and direction of solidification, in alloy systems such as Al-Cu, Al-Mg, Al-Zn, Al-Li, Al-Si, Al-Si-Cu, Cu-Zn, Pb-Sn, Sn-Pb and Steel. From these experiments it was determined that the primary dendritic spacing is a function of the temperature gradient, G, and the growth velocity, V, while the secondary and tertiary dendritic spacing are a function of the local solidification time, tSL. In the present work, we investigated the relation proposed by Hunt, Kurz and Fisher and by An and Liu in such alloy systems with dendritic growth, besides that, we correlated secondary and tertiary measured dendritic spacings with the equations proposed by Kattamis et. al., Allen and Hunt, Grugel and Feurer for the same alloy systems.

**3:10 PM**

**Large Refractory Metal Single Crystals Grown by Plasma-Induction Zone Melting**: *Viktor A. Shapovalov*[1]; [1]E.O. Paton Electric Welding Institute, 11 Bozhenko Str., Kiev 03680 Ukraine

The expanding applications of refractory metal single crystals has placed increasing demands on their properties and performance, especially concerning their enlargement and structural perfection. Due to their high melting point, the production of tungsten and molybdenum single-crystals is technically challenging. The growth of high quality crystals is critically dependent on the management of temperature profiles at the liquid-solid interface and the thermal fields in the solidified crystal. At the E.O. Paton Electric Welding Institute, a process for large crystal growth (a variant of the Verneuil method) has been developed. Special equipment for the production of large single crystal slabs of high purity and crystallographic perfection have been designed and installed. The crystal perfection is improved with the application of two independent heat sources (plasma-arc and induction) and process parameters have been optimized (principally, the ratio of plasma arc to induction heating power) in order to manage the thermal state during crystal growth and cooling. These parameters have been found to be the main factors controlling the production of high quality crystals. The plasma-arc source creates a local liquid pool of optimum form on the horizontally oriented seed crystal for the melting of the consumable materials (rods) for growth of the crystal in the shape of a slab. The choice of seed crystal orientation allows the control of material performance through the orientation dependence of properties in single crystals. The induction heater acts as a second independent heat source and acts to limit thermal losses as the slab grows. It effectively reduces the residual strains present in the crystals. Using the method described, single crystals of sizes up to 20 X 140 X 170 mm3 have been produced. Metallography and x-ray diffraction topography have been used for macro- and microstructural characterization of the single crystal slabs. Additionally, the large size of these crystals offers unique opportunities for measuring physical and mechanical properties.

**3:30 PM**

**Evolution of Recrystallization Texture in Drawn OFHC Copper Wire**: *Daudi R. Waryoba*[1]; Peter N. Kalu[1]; [1]National High Magnetic Field Laboratory, Matls. Sci. & Tech., 1800 E. Paul Dirac, Tallahassee, FL 32310 USA; [1]Florida State University, Mechl. Eng., National High Magnetic Field Lab., 1800 E. Paul Dirac, Tallahassee, FL 32310 USA

Oxygen free high conducting (OFHC) copper rod was drawn, at room temperature, to a true strain of 2.31 and annealed at various temperatures between 200∞C and 900∞C. Local orientations of the microstructures were measured by means of electron backscattered diffraction (EBSD) technique, from which inverse pole figures were calculated. The results of this study show that the starting, as-drawn, microtexture of the wire was a duplex <111>+<100> fiber texture. For annealing temperatures between 200∞C and 600∞C, a <111>+<112>+<100> fiber texture was formed. However, the intensity of <112> and <100> components were observed to increase at the expense of the <111> component. For annealing temperature between 600∞C and 800∞C, the intensity <111> component was observed to increase at the expense of the <100> and <112>. At 900∞C, the microtexture of the wire was essentially <111> fiber texture. It was concluded that the wire recrystallization texture of OFHC copper develops from the deformation texture. The volume fractions of the <111> and <100> depend on the annealing temperature. At low annealing temperature, the <100> component is enhanced due to depletion of the <111> component. At higher temperature, the <100> is unstable and is consumed by the <111> orientation. The <112> orientation is a transition component between the two major constituents. Thus, contrary to previous results that associated the <112> recrystallization texture with secondary recrystallization, the results of this study show that the <112> can also be formed at medium temperatures well before secondary recrystallization.

**3:50 PM Break**

**4:10 PM**

**Effect of Oxygen Content and Processing on Ti-6Al-4V Ti Alloy Combat Vehicle Components**: *Mustafa Guclu*[1]; Ibrahim Ucok[1]; Joseph R. Pickens[1]; [1]Concurrent Technologies Corporation, 100 CTC Dr., Johnstown, PA 15904 USA

Titanium (Ti) alloys are of interest to Army ground vehicle designers because of their unique combination of ballistic, corrosion and mechanical properties, such as high specific yield strength, fracture toughness and fatigue resistance. However, widespread use of Ti alloys has been limited by their relatively high cost compared to steels and aluminum alloys. Track components are good candidates for the application of titanium because the high specific strength and good fracture toughness of Ti alloys can be exploited to reduce the weight of moving parts. The use of single-melt Ti-6Al-4V combined with near-net shape processing technologies such as casting and forging can reduce fabrication cost even further. The Combat Vehicle Research (CVR) program at Concurrent Technologies Corporation (CTC) deals with cost reduction issues in fabrication of titanium components by using single melt titanium and simulating single melt titanium in manufacturing. In this study, Ti-6-4 track blocks were fabricated by rammed graphite, centrifugal investment casting, and open and closed die forging. The effects of oxygen level and processing method on mechanical properties were examined and compared to a standard Ti-6Al-4V alloy. Fabricated track blocks will be field-tested on the Marines Advanced Amphibious Assault Vehicle. The data presented in this paper will be useful to designers for assessing the viability of low-cost Ti-6Al-4V to reduce weight for combat vehicles. This work was conducted by Concurrent Technologies Corporation (CTC) for the Tank-automotive and Armaments Research Development & Engineering Center (TARDEC) through the National Center for Excellence in Metalworking Technology (NCEMT). CTC operates the NCEMT under Contract No. N00014-00-C-0544 to the US Navy as part of the US Navy Manufacturing Technology Program.

**4:40 PM**

**Microstructure and Deformation of Microalloyed Steels in the Two-Phase Region**: *Janusz Majta*[1]; Anna K. Zurek[2]; [1]University Mining & Metallurgy, Metall. & Matls. Sci., Mickiewicza 30, Krakow 30-059 Poland; [2]Los Alamos National Laboratory, MST-8, Los Alamos, NM 87545 USA

Traditionally conducted hot working processes with in depth knowledge and control of most important metallurgical phenomena are still very beneficial for achievement of high quality products for steels as long as the microalloyed elements are used. Recently developed technology of metal forming processes in the two-phase and ferrite regions, made it possible to enter new mechanical property characterization, controlled structure inhomogeneity and finally new implementations. To obtain these possibilities the computer control process of the full production technology is definitely needed. Thermomechanical processing strongly affects the microstructure components and the resultant mechanical properties of microalloyed steels. Therefore the influence of the process parameters on the microstructure and mechanical properties of niobium and boron treated steels has been investigated. The phenomena that have been taken into account are deformation temperature, amount of accumulated strain (both, in the austenite and ferrite phase), cooling rate during and after transformation, and dissolution of precipitates. For studying the microstructure development products that were formed in hot and intercritical conditions, rolling and compression tests were performed. The corresponding microstructures were investigated by means of TEM and optical microscopy. The obtained relationships, generalizing the problem, should optimize the technological parameters of the rolling, forging processes, considering obtaining the required distributions as well as average values of mechanical properties of final product. To reach the objective, the constitutive equations are proposed for modeling the effects of the hot-deformation process occurring in the austenite and two-phase region on the texture development of the resulting product. These models link advanced, finite element approaches simulating metal flow and heat transfer during hot-plastic deformation with constitutive equations describing microstructural processes, phase transformation and mechanical properties. Attention has so far been given to the calculation of the amount of transformed austenite and changes in temperature distributions.

**5:00 PM**

**Effect of an Heterogeneous Distribution of Dissolving Particles on the Formation of Banded Grain Structure in Wrought Alloys**: *SÈbastien Coste*[1]; Eric Andrieu[1]; Julitte Huez[2]; Olivier Brucelle[2]; [1]ENSIACET, CIRIMAT, 118 rte. de Narbonne, Cedex 4, Toulouse

31077 France; [2]Aubert & Duval Fortech, Service MÈtallurgie, 75 Blvd. de la LibÈration, Pamiers 09102 France

Alloy 718 is known to be sensitive to the interdendritic segregation forming during the ingot solidification. The occurrence of banded grain structures under heat treating conditions close to 1000∞C in relation with interdendritic segregation is often reported. In order to better understand this microstructural evolution, an extensive experimental program has been carried out. Finally, models based on selective dissolution of δ phase are proposed to account for these evolutions. The approach is detailed here after. In the first part of the present work, a grain growth simulation by Monte-Carlo method is proposed to illustrate the grain structure evolution in a banded particle distribution. However, the study of grain growth has shown that the banded structure can disappear under specifics heat treating conditions. Thus, in the second part of the study, a δ phase solutionning model is developed to point out the evolution of the δ fraction according to the local chemical composition and the heat treatment testing conditions.

**5:20 PM**

**Mutual Effects of Electro Slag Remelting and Open Die Radial Forging on the Properties of V-Microalloyed Steel**: Taha Mohamed Taha Mattar[1]; *Taher Ahmed El-Bitar*[1]; [1]CMRDI, Metal Forming, PO Box 87, Helwan, Cairo 11421 Egypt

Both ESR and forging processes have a pronounced effect on the steel properties. ESR process improves the properties of steel. The metal forming processes are not only used for dimensional purposes but also for enhancing the mechanical properties of steel. The present work aims at studying the mutual effects of both ESR and open die radial forging process on the mechanical properties and structure of V-microalloyed steel. In this study V-HSLA steel consumable electrodes were produced in an EAF. These electrodes were electro-slag remelted. The produced ingots were subjected to open die radial forging. Forging has been carried out to different amounts of reduction in cross-sectional area. The forged bars were subjected to both mechanical testing and microstructure investigations. The obtained data showed pronounced improvements in the microstructure and mechanical properties of produced steel.

## Materials Processing Under the Influence of Electrical and Magnetic Fields - IV

*Sponsored by:* Extraction & Processing Division, Materials Processing & Manufacturing Division, EPD-Process Fundamentals Committee, Jt. MPMD/EPD-Process Modeling Analysis & Control Committee

*Program Organizers:* Joanna R. Groza, University of California-Davis, Chemical Engineering Material Science Department, Davis, CA 95616 USA; George S. Dulikravich, The University of Texas at Arlington, Multidisciplinary Analysis, Inverse Design, and Optimization (MAIDO) Program, Department of Mechanical and Aerospace Engineering, Arlington, TX 76019 USA; Nagy H. El-Kaddah, University of Alabama, Department of Metallurgical & Materials Engineering, Tuscaloosa, AL 35487-0202 USA; James W. Evans, University of California, Department of Materials Science and Mineral Engineering, Berkeley, CA 94720 USA; Zuhair Munir, University of California, College of Engineering, Davis, CA 95616-5294 USA; Srinath Viswanathan, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6083 USA

Tuesday PM — Room: 14A
March 4, 2003 — Location: San Diego Convention Center

*Session Chair:* Srinath Viswanathan, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6083 USA

**2:30 PM Workshop**

**3:15 PM Workshop on the Influence of External Fields on Materials Processing: Schedule TBA**

**4:00 PM Workshop on Electrical and Magnetic Field Effects in Materials Processing Invited speaker: Dr. K. L. Murti (NSF)**

**4:45 PM Break**

## Materials Prognosis: Integrating Damage-State Awareness and Mechanism-Based Prediction: Damage Interrogation

*Sponsored by:* Structural Materials Division,

*Program Organizers:* James M. Larsen, US Air Force, Air Force Research Laboratory, Materials and Manufacturing Directorate, Wright-Patterson AFB, OH 45433-7817 USA; Leo Christodoulou, Defense Advanced Research Agency, Arlington, VA 22203-1714 USA; William J. Hardman, Naval Air Systems Command, Propulsion and Power Directorate (AIR 4.4.2), Patuxent River, MD 20670-1534 USA; Andrew J. Hess, Naval Air Systems Command, Propulsion and Power Directorate, Patuxent River, MD 20670-1534 USA; J. Wayne Jones, University of Michigan, College of Engineering, Department of Materials, Science and Engineering, Ann Arbor, MI 48109 USA; Stephan M. Russ, Air Force Research Laboratory, Materials and Manufacturing Directorate, AFRL/MLLN, Wright-Patterson Air Force Base, OH 45433-7817 USA

Tuesday PM — Room: 16A
March 4, 2003 — Location: San Diego Convention Center

*Session Chairs:* William J. Hardman, Naval Air Systems Command, Propulsion & Power Direct., Patuxent River, MD 20670-1534 USA; Reji John, Air Force Research Laboratory, AFRL/MLLMN, WPAFB, OH 45433-7817 USA

**2:00 PM**

**Nonlinear Acoustics and X-Ray Diffraction for Evaluation of the Fatigue Damage-State in Ti-6Al-4V**: *Shamachary Sathish*[1]; Jerome Frouin[1]; [1]University of Dayton Research Institute, 300 College Park, Dayton, OH 45469-0127 USA

Nonlinear acoustics and x-ray diffraction techniques have been used to study the changes in the local properties in fatigue-fractured samples of Ti-6Al-4V. Large changes in the nonlinear acoustic parameter and the x-ray diffraction peak width have been observed as the fracture end is approached. The role of changing microstructure and the dislocation density due to cyclic loading will be utilized to explain the experimental observations. Application of the experimental methods for the detection of the onset of fatigue damage and its implication on the prognostication of fatigue cracks are discussed.

**2:30 PM Invited**

**Material Characterization and Life Prediction for Critical Components Through Application of Photon Induced Positron Annihilation (PIPA)**: *Douglas Akers*[1]; [1]Positron Systems, Inc., 6151 N. Discovery Way, Boise, ID 83713 USA

A new patented technology, Photon Induced Positron Annihilation (PIPA) has been developed that provides a revolutionary damage prognosis capability to nondestructively detect all types of failure mechanisms such as fatigue, creep, and radiation induced damage, at levels less than 1% change in the atomic lattice structure. Further, PIPA can accurately assess existing defect levels and predict the remaining life of various metallic, composite, and polymeric materials. PIPA has successfully detected microstructure fatigue mechanisms and crack growth phenomena in numerous materials, such as aluminum and super nickel alloys, stainless steel and titanium. This technology has numerous applications in the power generation and aerospace industries from the assessment of high temperature creep in steam piping to fatigue and compressive stress release characterization on aircraft jet engine fan disks and turbine blades. Additionally, PIPA has demonstrated the capability to detect damage in 2nd layer materials, without disassembly; demonstrating in situ interrogation capability.

**2:55 PM**

**Scattered Light Scanning for Fatigue Damage Precursor Detection on Turbine Components**: *James C. Earthman*[1]; [1]University of California-Irvine, Cheml. Eng. & Matl. Sci., Eng. Tower 916, Irvine, CA 92697-2575 USA

A technique for in-situ laser light scanning (LLS) was developed to monitor surface damage on nickel-base superalloy turbine component under low-cycle fatigue conditions. This technique characterizes the surface state using the defect frequency parameter which was designed to minimize memory requirements and data processing time. As a result, the present technique is capable of scanning speeds that are substantially greater than those achieved with image processing methods. Sections of Inconel 718 turbine rotors were tested using a servo-hydraulic MTS machine at ambient temperature under load control conditions. The fatigue damage was monitored by scanning a laser beam along the rotor section in situ and during periodic interruptions of the cyclic loading. Acetate replicas of the gage section surface were also made to examine the surface mrophology using SEM. Comparisons of the results demonstrate the capabilities of the present light scanning technique for characterizing fatigue damage precursors on the surface of turbine components. In particular, a rapid rise in the mean defect frequency is shown to correspond to surface relief features that correspond to grain boundaries that intersect the surface in the areas of greatest stress. The presence of this surface relief can be attributed to the presence of relatively soft precipitate free zones along the grain boundaries that preferentially deform under fatigue loading conditions leading to the formation of microcracks.

**3:20 PM Break**

**3:50 PM**
**Nondestructively Estimated Damage Degradation in Ceramic Matrix Composites**: *Chris Deemer*[1]; Benjamin J. Wheeler[1]; William A. Ellingson[1]; [1]Argonne National Laboratory, Energy Tech. Div., 9700 S. Cass Ave., Argonne, IL 60439 USA

In ceramic matrix composites (CMC), the ability to quantify damage caused by unpredictable loading has been a goal for some time. Recently, an acousto-ultrasonic technique to nondestructively measure a damage parameter for monitoring matrix cracking in CMC materials has been developed. Data has been obtained on damaged Melt Infiltrated (MI) SiC/SiC and oxide/oxide CMC materials. Damage has been induced by using tension-tension cyclic fatigue, monotonic tensile loading, as well as thermal cycling and impact testing. Details of the NDE method and review the results are presented. Work supported by US DOE/EERE/OIT-CFCC Program under contract W-31-109-Eng-38.

**4:15 PM**
**Ball Indentation for Nondestructive Monitoring of Thermal Aging of Cast Stainless-Steel (CF-8) and Alloy 625**: *K. L. Murty*[1]; M. D. Mathew[2]; [1]North Carolina State University, 2500 Stinson Dr., PO Box 7909, Raleigh, NC 27695-7909 USA; [2]Indira Gandhi Center for Atomic Research, Kalpakkam 603102 India

Monitoring the progressive changes in the mechanical properties of high temperature materials in-service is important for ensuring the structural integrity of the components and also for possible extension of their useful service life. In this paper, we describe an innovative automated technique based on ball indentation that can be used for laboratory and field applications in order to measure the mechanical and fracture properties of materials along with typical results from laboratory studies on engineering materials. Thermal aging effects are considered in CF-8 stainless steel and a superalloy 625. Ball indentation test results are compared with those obtained from traditional tensile and fracture tests, and are correlated with the microstructural modifications due to thermal aging. Plausible extensions for in-service applications will be described. K.L. Murty is currently Program Director, Metals Research, DMR, National Science Foundation.

**4:40 PM**
**Piezoelectric In-Situ Transmission Electron Microscopy Observations of Fatigue Damage Accumulation in Constrained Metallic Thin Films**: X. Tan[1]; P. Liu[1]; *J. K. Shang*[1]; [1]University of Illinois at Urbana-Champaign, Dept. of Matls. Sci. & Eng., 1304 W. Green St., Urbana, IL 61801 USA

A piezoelectric in-situ transmission electron microscopy (TEM) technique has been developed to observe damage mechanism in constrained metallic thin films under cyclic loading. The technique was based on the piezoelectric actuation of a multilayered structure in which a metallic thin film was sandwiched between a piezoelectric actuator and a silicon substrate. An alternating electric field with a static offset was applied on the piezoelectric actuator to drive the crack growth in thin metallic layer while the sample was imaged in TEM. The technique was demonstrated on solder thin films where cavitation was found to be the dominant fatigue damage mechanism.

**5:05 PM**
**Mechanism-Based Models for the Prediction of Fatigue in Si MEMS Structures**: Seyed Allameh[1]; M. Huang[1]; P. Shrotriya[2]; Y. Cao[1]; Z. Suo[1]; *W. O. Soboyejo*[1]; [1]Princeton University, Princeton Matls. Inst., D404 E. Quad., Princeton, NJ 08544 USA; [2]Brown University, Div. of Eng., Providence, RI 02912 USA

This paper presents mechanism-based models for the prediction of fatigue in silicon micro-electro-mechanical systems (MEMS) structures. Following a brief review of the experimental evidence of fatigue, the paper identifies the important role of the topical $SiO_2$ layer on fatigue in silicon MEMS structures. Mechanism-based models are then used to model the different stages of environmentally-assisted fatigue under cyclic and static loading. These include: activation volume-based models for the prediction of surface roughening and crack nucleation; fatigue crack growth and stress corrosion cracking models for the prediction of crack growth, and bi-layer fracture models for the modeling of final failure conditions. The implications of the results are then discussed for the design of reliable Si MEMS structures.

## Measurement and Interpretation of Internal/ Residual Stresses: Processing

*Sponsored by:* Structural Materials Division, ASM International: Materials Science Critical Technology Sector, Materials Processing & Manufacturing Division, SMD-Mechanical Behavior of Materials-(Jt. ASM-MSCTS), MPMD-Shaping and Forming Committee
*Program Organizers:* Craig S. Hartley, Air Force Office of Scientific Research, Arlington, VA 22203 USA; Mark A.M. Bourke, Los Alamos National Laboratory, Neutron Science Center, Los Alamos, NM 87545 USA; Bimal K. Kad, University of California, Ames Laboratory, La Jolla, CA 92093-0085 USA

Tuesday PM          Room: 17B
March 4, 2003       Location: San Diego Convention Center

*Session Chairs:* Tom Holden, Los Alamos National Laboratory, Eng. Sci. Applic. Design Eng., Los Alamos, NM 87545 USA; Camden R. Hubbard, Oak Ridge National Laboratory, Metals & Ceram. Div., Oak Ridge, TN 37830-6064 USA

**2:00 PM**
**Residual Stress Relaxation in Fatigue of Mechanically Surface Treated Materials**: *I. Altenberger*[2]; U. Noster[2]; R. K. Nalla[1]; B. Scholtes[2]; R. O. Ritchie[1]; [1]University of California-Berkeley, Matls. Sci. & Eng., Berkeley, CA 94720 USA; [2]Institut fuer Werkstofftechnik, Un. Kassel, Kassel 34125 Germany

A necessary prerequisite for the effectiveness of mechanical surface treatments in enhancing the fatigue properties of a material is the mechanical and thermal stability of near-surface residual stresses or microstructures. Only stable residual stresses influence fatigue strength/ life and are usually regarded as local mean stresses. Additionally, near-surface microstructures, such as those associated with increased dislocation densities, strongly influence fatigue performance of mechanically surface treated materials; however, the interactions between the residual stresses and near-surface microstructures are rarely investigated. It is the objective of this paper to clarify the role of fatigue loading parameters, such as the stress amplitude and plastic strain amplitude as well as that of the surface treatment induced microstructures, in the relaxation of macro- and micro residual stresses during mechanical and thermal cycling. Characteristic examples of fatigue-induced residual stress relaxation in various metallic engineering alloys, including steels, titanium and magnesium alloys, are presented and recommendations for optimizing the stability of the residual stresses are proposed.

**2:30 PM Invited**
**An Investigation of Springback Stresses in Sheet Metal Forming**: *Thomas Gnaeupel-Herold*[1]; Henry Prask[1]; [1]NIST, Ctr. for Neutron Rsrch., 100 Bureau Dr., Stop 8562, Gaithersburg, MD 20899 USA

Springback is the shape change of sheet metal after forming and removal from the die. In order to achieve sufficiently small product tolerances, conventional die design involves expensive, time-consuming trial-and-error methods which represent major challenges in the cost-effective manufacturing of lightweight and fuel efficient vehicles. In the Springback Predictability Project there is a joint effort underway involving car companies, material suppliers and government agencies to develop a 3D computer model to predict stress, strain and fracture in sheet metal with the goal of a significant reduction in tool design time. The necessary data for understanding the forming process is being collected. Springback is an effect of residual stresses that are caused by different levels of accumulated plastic strain through the thickness of sheet metal. Upon release from the die, these stresses create a bending moment which is essentially the integrated through-thickness stress. The computer model is benchmarked by these stresses which are, in turn, benchmarked by the bending moment that can be measured my mechanical means. In a simplified approach, both modeling and measurement of springback stresses is focused on deep drawn cups after die removal and trimming of top and bottom of the cup. Through-thickness axial and hoop stresses were measured on Al-6022 and steel for wall thicknesses ranging from 0.9 mm to >3 mm and for different locations axially and around the cup circumference by means of synchrotron radiation and neutron diffraction. Spatial resolutions varied, depending on thickness, from 0.05 mm up to 0.5 mm. It was found that the through-thickness hoop stresses deviate distinctively from the symmetric S-profile sometimes assumed in simulations. We also obtained results indicating substantial stress variations in the axial direction. An update on the status of the predictability project will be given.

**3:00 PM**
**Mapping Complex Residual Stresses in a Large, Cold Worked, Aluminum Forging**: *Michael B. Prime*[1]; [1]Los Alamos National Laboratory, Eng. Scis. & Applic. Div., MS P946, Los Alamos, NM 87545 USA

Distortion in high-strength aluminum forgings has been an extremely costly problem for aerospace manufacturers. The distortion is caused when residual stresses are released as the part is machined to its final dimensions. The problem occurs because the complex cold compression process that is used to relieve quenching residual stresses in the forgings is not sufficiently effective. In this study, the residual stresses before and after cold compression of a large (107x158x718 mm) 7050-T74 forging were mapped using the contour method. The results show a spatially periodic variation of stresses that results from the periodic nature of the cold work. The results compare favorably with a finite element prediction of the stresses. The reasons why the stress relief process is not successful, compared to the stretching process used for plate, is discussed. Also discussed is why the residual stress measurements probably would not have been possible with any method other than the contour method.

**3:20 PM**
**Modeling and Measurement of Temper Stresses in Bulk Metallic Glasses**: *Cahit Can Aydiner*[1]; Ersan Ustundag[1]; Michael B. Prime[2]; [1]California Institute of Technology, Matls. Sci., 1200 E. California Blvd., MC 138-78, Pasadena, CA 91125 USA; [2]Los Alamos National Laboratory, Eng. Scis. & Appl. Div., Los Alamos, NM 87545 USA

New multi-component metallic alloys with exceptional glass forming ability have recently been developed at Caltech. These alloys allow the processing of large amorphous specimens. The possibility of formation of thermal-tempering-induced residual stresses during the processing of these bulk metallic glass specimens was investigated via several models. In particular, the viscoelastic nature of the material was considered. The crack compliance method was then used to measure the residual stress profiles. The measured profiles were roughly parabolic suggesting that thermal tempering was the dominant residual stress generation mechanism. It was shown that material properties and processing conditions exert strong influence on the final residual stress values.

**3:40 PM**
**Microstrain Evolution During Creep of a Polycrystalline Superalloy**: S. Ma[1]; D. Brown[2]; B. Clausen[2]; M. Bourke[2]; B. S. Majumdar[1]; [1]New Mexico Tech, Matls. Dept., Socorro, NM 87801 USA; [2]Los Alamos National Laboratory, Los Alamos, NM 87545 USA

The creep resistance of superalloys containing a high volume fraction of gí phase is strongly influenced by lattice misfit, and by constraints imposed on the narrow g channels by the primarily non-deforming gí precipitates. In order to probe deformation behavior at the g/gí level, we have conducted creep experiments at 900C on a polycrystalline superalloy CM247LC. A pulsed neutron diffraction source was used to capture the insitu *d*//bsb/*hkl*//esb/ and appropriate procedures were developed to deconvolute the phase strains. The elastic misfit was negligible at room temperature, but increased to a significant negative value at 900 C, consistent with estimates based on thermal strain calculations. During creep, the evolution of microstrains was a function of grain orientation, and could be categorized in terms of location within the stereographic triangle. For example, grains with the loading axis close to the [001] orientation exhibited a monotonic increase in elastic microstrain in the gí phase as a function of creep time. In contrast, the corresponding g-phase exhibited a *decrease* in microstrain during the tertiary creep stage. We rationalize this latter behavior in terms of a build up of interface dislocations in the vertical g channels. While such interface dislocations have sometimes been observed in the past, this work likely provides the first data validating stresses arising from such a dislocation network. These stresses are important, because microstructural rafting, which is a major reason for loss of creep resistance at high temperatures, is driven by unequal strain energy in the horizontal and vertical g channels. This work was supported through contract UCDRD-10012. We thank the SMARTS LANSCE center for the neutron diffraction experiments

**4:00 PM Break**

**4:15 PM**
**Process Optimization Through Measurement and Monitoring of Residual Stresses Under Industrial Conditions**: *Prabir K. Chaudhury*[1]; [1]Intercontinental Manufacturing, 1200 N Glenbrook Dr., Garland, TX 75040 USA

Residual stresses play a very important role in manufacturing processes of structural parts. Monitoring and control of the residual stresses induced by various industrial metalworking processes are important for reducing cost of many structural aerospace parts. This investigation focuses on a commercial aircraft part to demonstrate the process optimization for reducing residual stresses through measurement of residual stresses by machining and x-ray diffraction techniques. First, the heat treatment process was optimized to reduce residual stresses without significantly sacrificing mechanical properties. Then various methods of residual stress relieving was conducted and the residual stresses were monitored to determine their effectiveness. Distortion measurement after machining an area of a forged and heat treated aluminum part was primarily used as a measure of residual stresses. Some of the distortion measurments were compared and verified with data from x-ray diffraction measurements.

**4:35 PM**
**Residual Stresses in Components Made by the Laser-Engineered Net Shaping (LENS™) Process**: *Partha Rangaswamy*[1]; Thomas M. Holden[1]; Ronald B. Rogge[2]; Michelle L. Griffith[3]; Michael B. Prime[1]; [1]Los Alamos National Laboratory, Eng. Sci. Applic., Design Eng., Los Alamos, NM 87545 USA; [2]National Research Council of Canada, Neutron Prog. for Matls. Rsrch., Chalk River Labs., Chalk River, Ontario K0J 1J0 Canada; [3]Sandia National Laboratory, Albuquerque, NM 87185 USA

During manufacturing of components using the Laser Engineered Net Shaping (LENSô) process the introduction of residual stresses is a problem associated with cracking for volumes greater than 100 $cm^3$. The origin is attributed to thermal transients encountered during solidification. In the absence of predictive models measurements are imperative. Preliminary measurements using a Laser Holographic Drilling Technique (holographic) on 316 stainless steel specimens have shown yield level tensile residual stresses. However, the holographic technique is restricted to near surface measurements (<1 mm), accordingly we used neutron diffraction to probe greater depths (25-50 mm). Residual stresses were measured in LENSô samples (316 Stainless Steel) having simple geometrical shapes. Using the L3 spectrometer at Chalk River Laboratories (Canada), stresses were mapped spatially with sampling volumes ranging from 2 to 10 $mm^3$ in three orthogonal directions. The neutron (core) and holographic (surface) results will be compared and discussed in the contest of growth direction during the LENS process. These results will also be compared against residual stresses obtained using contour method, which provides spatial distribution normal to the plane of sectioning.

**4:55 PM Invited**
**Shot-Peen Residual Stress Relaxation and its Application in Life Management of Turbine Engine Components**: *Reji John*[1]; James M. Larsen[1]; Mark P. Blodgett[2]; Stephan M. Russ[1]; Jeffrey Finch[1]; Bryan Sanbongi[2]; [1]US Air Force Reseach Laboratory, AFRL/MLLMN, Matls. & Mfg. Direct., WPAFB, OH 45419 USA; [2]US Air Force Research Laboratory, AFRL/MLLP, Matls. & Mfg. Direct., WPAFB, OH 45433-7817 USA

The US Air Force has initiated a technology development initiative known as Engine Rotor Life Extension (ERLE), which has the goal of extending the useful lifetime of major, fracture-critical components in gas turbine engines, without increasing the fleet-wide risk of component failure. Current damage-tolerance based life management practices do not explicitly account for the beneficial effects of shot-peen residual stresses. This presentation will critically assess the role of residual stresses in the durability of representative turbine engine materials and identify opportunities for improvement in life prediction methods. Recent studies have shown that residual stresses in engine components relax during service. Typically, this relaxation effect occurs across the entire residual stress profile. Hence, reliable NDE techniques are required to measure the residual stress profile during inspections. This presentation will discuss the life prediction and NDE issues to be considered prior to incorporation of residual stresses in engine component life management practices.

**5:15 PM**
**The Effects of Shot Peening Surface Coverage on the Residual Stress of Fretting Fatigued Ti-6Al-4V Samples**: *Sonia Aixa Martinez*[1]; Shamachary Sathish[2]; Mark P. Blodgett[1]; Shankar Mall[3]; [1]Air Force Research Laboratory, Matls. & Mfg. Direct., 2230 Tenth

St., Ste. 1, WPAFB, OH 45433-7817 USA; [2]University of Dayton Research Institute, Structl. Integrity & Non Destructive Evaluation, 300 College Park, Dayton, OH 45469-0127 USA; [3]Air Force Institute of Technology, Eng. Dept., WPAFB, OH 45433-7765 USA

Residual stresses generated by shot peening are compressive in nature. The depth of these stresses is a function of the peening intensity. Increasing the peening intensity generates a deeper layer of compressive stresses, this is desirable for crack growth resistance and fatigue life. Optimum residual stress distribution can be obtained if there is an understanding of the effect of shot peening parameters. The effect of shot peening surfaces under fretting wear is of importance in this research. Fretting is a contact loading that modifies the surface of the component and can lead to relaxation of the compressive residual stresses and loss of matter. In this investigation, the effects of fretting fatigue on the residual stress distribution and fatigue life of Ti-6Al-4V shot peened samples have been studied. Experiments are conducted in dry conditions for samples made with different surface coverages. X-ray diffraction has been used as a method for measuring surface residual stress.

## Microstructural Processes in Irradiated Materials: Multiscale Modeling II

*Sponsored by:* Structural Materials Division, ASM International: Materials Science Critical Technology Sector, SMD-Nuclear Materials Committee-(Jt. ASM-MSCTS)
*Program Organizers:* Lance L. Snead, Oak Ridge National Laboratory, Metals and Ceramics Division, Oak Ridge, TN 37830-6138 USA; Charlotte Becquart, Universite de Lille I, Laboratoier de Metallurgie Physique Et Genie des Materiaux, Villenueve síAscq, Cedex 59655 France

Tuesday PM　　Room: 11A
March 4, 2003　　Location: San Diego Convention Center

*Session Chairs:* Yuri Osetsky, The University of Liverpool, Dept. of Eng., Brownlow Hill, Liverpool L69 3GH UK; Charlotte Becquart, Universite de Lille I, Lab. de Metallurgie Physique et Genie des Materiaux, Villenueve síAscq, Cedex 59655 France

**2:00 PM**
**1-D to 3-D Diffusion Reaction Kinetics of Cascade Induced SIA Clusters in MetalsñImplications for Void Nucleation and Growth**: *Helmut Trinkaus*[1]; Bachu N. Singh[2]; [1]ESS Project, Forschungszentrum J¸lich, J¸lich D-52425 Germany; [2]Risoe National Laboratory, Matls. Rsrch. Dept., Roskilde 4000 Danemark

It has been shown recently that some features in the microstructural evolution occurring in metals under cascade damage can be rationalised in terms of intra-cascade clustering of vacancies and self-interstitial atoms (SIAs), differences in the thermal stability and mobility of the resulting clusters and one-dimensional (1-D) glide of SIA clusters. We discuss consequences of deviations of SIA cluster diffusion from strictly 1-D, resulting in diffusion reaction kinetics between the 1-D and 3-D limiting cases. Analytical solutions for the partial sink strengths of voids and dislocations for the annihilation of SIA clusters in such general reaction kinetics are presented. An intermediate kinetics is identified where the sink strength increases continuously with increasing disturbance from low values for 1-D to high values for 3-D. The implications of such changes in the SIA cluster reaction kinetics, particularly for enhanced swelling near grain boundaries and saturation of void growth, are discussed.

**2:45 PM**
**Meaning, Relationship and Influence of Interaction Radii Used in Rate Theory and Kinetic Monte Carlo Modelling of the Clustering of Point Defects**: Christophe Domain[3]; Charlotte S. Becquart[2]; *Alain Barbu*[1]; [1]CEA, LSI, Ecole Polytechnique, Palaiseau F-91128 France; [2]LMPGM, UMR 8517, UniversitÈ de Lille 1, Villeneuve díAscq F-59655 France; [3]EDF R&D, MMC, Moret sur Loing F-77250 France

One of the key parameter in modelling the nucleation and growth of point defect clusters in rate theory as well as in lattice Kinetic Monte Carlo (KMC) is the interaction radius (recombination or clustering radius). Depending upon the model used, the meaning of this radius is rather different. In lattice KMC, defects migrate from a lattice site to a nearest neighbour site through jumps characterised by jump frequencies, the interaction radius is the critical discrete distance (which can depend on the relative crystalline direction) below which an instantaneous reaction occurs. In rate theory, the defects migration is no more described in terms of jumps but by diffusion coefficients which are more global quantities. As a consequence, the physical meaning of the capture radius is not straightforward. The reason is that it takes into account the different paths that the defects can follow to get close to each other at the atomic level. This point will be illustrated by KMC and rate theory simulations of electron irradiations in pure Fe. These simulations will be compared to experiments carried out with 2.5 MeV electrons.

**3:05 PM**
**Ab Initio Contribution to the Study Interaction of Point Defects with Interstitial Impurities (C, N) in Fe**: Christophe Domain[2]; *Charlotte S. Becquart*[1]; [1]UniversitÈ de Lille I, LMPGM, UMR 8517, Batiment C6, Villeneuve díAscq, CÈdex 59655 France; [2]EDF-R&D, MMC, Les RenardiËres, Moret sur Loing F-77818 France

The critical importance of interstitial impurities in bcc metals has been observed over many years and is now well established. Under irradiation, the defects produced appear to serve as trapping centres for these interstitial impurities and as a consequence the mechanical properties of the materials are affected. We have investigated, by ab initio calculations based on the density functional theory, the interactions of C and N atoms with point defects in Fe. The structures and relative stabilities of the different configurations as well as their formation and binding energies have been determined. The consequences of the results are discussed.

**3:25 PM Break**

**3:55 PM**
**Sink Strengths Revisited**: N. V. Doan[1]; G. Martin[1]; J.-L. Bocquet[1]; *J. Dalla Torre*[1]; [1]CEA Saclay, DMN/SRMP, Bat. 520, Gif-sur-Yvette 91191 France

The rate theory of irradiation effects in crystalline solids rests on a set of two ordinary differential equations which, for each type of point defect (vacancy and self-interstitial), describe the balance between the production of defects and their annihilation. The elimination rate on point defect sinks is proportional to the defect concentration times the defect diffusion coefficient times a geometrical factor, the ìsink strengthî. We propose a new criterion to define the sink strength: the value of the sink strength should give the correct value for the partitioning of the defect annihilation between mutual recombination and elimination on sinks. Depending on the irradiation conditions, the correcting factor on individual sink strengths may be large (several orders of magnitude). When several types of sinks compete, the sink strengths, as defined in this work, are additive, at variance with the classical ones.

**4:15 PM**
**Modeling Structural Metastability of Irradiated Thin Films**: Paolo M. Ossi[1]; *Alessio Lamperti*[1]; [1]Politecnico, Dip. Ingegneria Nucleare, via Ponzio, 34/3, Milano 20133 Italy

The experimentally observed structure evolution in irradiated binary compounds, both metallic and non-metallic, where dense collision cascades form, is modelled by the Segregation-Charge Transfer (SCT) atomistic model. The cascade space and time evolution produces non-equilibrium compositional and electronic density profiles at the cascade-crystalline matrix interface. This is due to short-range interface migration of one film constituent. System relaxation to metastable equilibrium is simulated by charge transfer reactions (CTR), each involving a couple of dissimilar atoms of the initial compound (IC), that generate an effective compound (EC) dimer. By SCT model we calculate the energy cost to insert an EC dimer into the matrix, the formation enthalpy difference between corresponding EC and IC, and the local volume change the film undergoes when a CTR results in ion formation. For the above structure stability parameters threshold values provide a qualitative separation between amorphised and crystalline compounds, both metallic and non-metallic.

## Phase Stability, Phase Transformations & Reactive Phase Formation in Electronic Materials - IV

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

*Program Organizers:* Sinn-Wen Chen, National Tsing-Hua University, Department of Chemical Engineering, Hsinchu 300 Taiwan; C. Robert Kao, National Central University, Department of Chemical and Materials Engineering, Chungli City 32054 Taiwan; Hyuck Mo Lee, Korea Advanced Institute of Science & Technology, Department of Materials Science & Engineering, Taejon 305-701 Korea; Suzanne E. Mohney, Pennsylvania State University, Department of Materials Science & Engineering, University Park, PA 16802 USA; Michael R. Notis, Lehigh University, Department of Materials Science and Engineering, Bethlehem, PA 18015 USA; Douglas J. Swenson, Michigan Technological University, Department of Materials Science & Engineering, Houghton, MI 49931 USA

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| Tuesday PM | Room: 12 |
| March 4, 2003 | Location: San Diego Convention Center |

*Session Chairs:* Hyuck Mo Lee, Korea Advanced Institute of Science and Technology, Dept. of Matls. Sci. & Eng., Taejon 305-701 Korea; Sinn-Wen Chen, National Tsing Hua University, Dept. of Cheml. Eng., Hsinchu 300 Taiwan

**2:00 PM Invited**
**Morphology Transition of Interfacial Intermetallic Compound at Sn-3.5Ag/Ni Interface**: Jong Hoon Kim[1]; *Hyuck Mo Lee*[1]; [1]Korea Advanced Institute of Science and Technology, Dept. of Matls. Sci. & Eng., Kusung-Dong 373-1, Yusung-Gu, Taejon 305-701 Korea

The morphology transition of Ni3Sn4 grains that formed at the interface between liquid Sn-3.5Ag (in wt.%) solder and Ni substrate has been observed at 650°C. This morphology transition of Ni3Sn4 is caused by decrease of enthalpy of formation of Ni3Sn4 phase and explained well through Jacksonís parameter. The solder joint strength with increase of soldering temperature decreased rapidly at around 6.5 micrometer thick IMC. However the solder joint strength with increase of soldering time decreased slowly without drop of solder joint strength although the thickness of IMC is larger than 6.5 micrometer. The drop of solder joint strength with increase of soldering temperature appears to be due to a large width of IMC grains.

**2:20 PM Invited**
**The Morphology and Kinetics of Solid-State Intermetallic Compound Layer Growth Between Copper and Sn-Ag-XCu Solders (X = 0, 0.6, 4.0)**: *Paul Thomas Vianco*[1]; Jerome A. Rejent[1]; Paul Hlava[1]; [1]Sandia National Laboratories, MS0889, PO Box 5800, Albuquerque, NM 87185-0889 USA

The morphology and kinetics of interfacial, solid-state intermetallic compound layer growth are a function of compositions of the solder and base metal members of the couple. These properties were examined for Sn-based solders containing 0.6Cu (wt.%) or 4.0Cu, which were applied to 100Cu base metal by the hot solder dipping process. Aging was performed for time periods of 1-400 days and at temperatures of 70-205∞C. The 100Sn/Cu couples provided the baseline. The interface reaction kinetics were determined, based upon Arrhenius format. Electron microprobe analysis (EMPA) identified Cu3Sn and Cu6Sn5 sub-layers, the extents of which were dependent upon the particular solder composition. Understanding the mechanism that varies the Cu3Sn/Cu6Sn5 ratio is required for computational model development for these systems. Sandia is a multi-program laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the US Dept. of Energy under contract DE-AC04-94AL85000.

**2:40 PM Invited**
**Reduced Melting Temperatures in Nanometer Length Scale Eutectic Alloys**: Elisa Pueschel[1]; Richard Chromik[1]; Mitchell Johnson[1]; Natalya Chernova[1]; Scott Oppenheimer[1]; *Eric J. Cotts*[1]; [1]SUNY Binghamton, Physics & Matls. Sci., Sci. 2, PO Box 6016, Binghamton, NY 13902-6016 USA

Melting temperatures in eutectic alloys were examined as a function of relevant length scales. Thin film composites were fabricated by physical vapor deposition. Average compositions of these multilayered structures were near eutectic, or far from eutectic. The structure of the composites was examined by x-ray diffraction analysis and electron microscopy. Melting behavior was studied using differential scanning calorimetry. Reduced eutectic melting temperatures were observed in a number of systems, including Al-Sn and Au-Si. Support of the National Science Foundation, DMR 9902783 is gratefully acknowledged.

**3:00 PM**
**Sputtered Copper Films with Insoluble Elements for Cu Metallization: A Thermal Annealing Study**: Chon-Hsin Lin[1]; *J. P. Chu*[1]; [1]National Taiwan Ocean University, Inst. of Matls. Eng., No. 2 Pei-Ning Rd., Keelung 202 Taiwan

Copper is an attractive material for metallization in microelectronics, owing to its low resistivity and high reliability against electromigration compared with Al and its alloys. However, Cu diffuses readily into Si and SiO2, resulting in the formation of copper silicide compounds at low temperatures. This work was directed towards the study of thermal stability, microstructure and electrical properties of Cu films containing dilute insoluble W or C. Cu-11.3at.%C and Cu-2.3at.%W films deposited on Si(100) substrate by R.F. magnetron sputtering were annealed at temperatures ranging from 200 to 800∞C. As-deposited Cu-C and Cu-W films consisted of non-equilibrium solid solutions of C in Cu with nanocrystalline microstructures. X-ray diffraction results show that Cu4Si is formed at 530∞C that is better than pure Cu film, which appears at 400∞C. This result is consistent with transmission and scanning electron microscopy observations and implies that the amount C and W could inhibit formation of Cu4Si compound. With the insoluble W for retardation effect, the film also maintains its fine structure after annealing up to 400∞C. On the contrary, the pure Cu film has suffered adverse recrystallization and reaction with Si substrate at 400∞C. Thermal stability of Cu-C and Cu-W films will be presented and discussed in the light of the results obtained.

**3:15 PM**
**Electromigration in SnAg3.8Cu0.7 Solder Lines**: *K. C. Lin*[1]; Ying-Chao Hsu[1]; T. L. Shao[1]; C. Chen[1]; [1]National Chiao Tung University, Dept. of Matls. Sci. & Eng., 1001 Ta Hsueh Rd., Hsinchu 300 Taiwan

Due to the excellent thermo-mechanical property, SnAg3.8Cu0.7 solder will be one of the most promise lead-free solders in microelectronic packaging industry. This study investigated the electromigration damage on lead-free SnAg3.8Cu0.7 solder in V-groove lines. V-groove lines were obtained on (001) Si wafers by anisotropic etching. Metallurgy layers of Cr/Cu/Au were deposited by e-beam evaporation. Nickel film were electroplated to form electrodes. V-grooves were finally filled with SnAg3.8Cu0.7 solder by reflowing the solder into the lines. Electromigration damage were investigated by applying current through the v-groove lines under a current density of $2*10^4$ A/cm2 at 100°C. Compounds of (Cu, Ni)6Sn5 were observed at the interface between the solder and the Ni electrode after reflow. After current stressing for seven days, copper content in (Cu, Ni)6Sn5 compound decreased. Also, Ni atoms were carried into the solder and reacted with tin atoms to form Ni3Sn4. Whiskers and hillocks were observed at the anode side, and voids were observed at the cathode side.

**3:30 PM Break**

**3:50 PM Invited**
**Intermetallic Formation and Growth Around Metallic Particles in Sn-Based Solders**: H. Rhee[1]; K. C. Chen[2]; J. G. Lee[1]; *K. N. Subramanian*[1]; [1]Michigan State University, Dept. of Cheml. Eng. & Matls. Sci., E. Lansing, MI 48824-1226 USA; [2]California Polytechnic State University, Matls. Eng. Dept., San Luis Obispo, CA 93407 USA

Incorporation of metallic particulate reinforcements in Sn-base solder has resulted in intermetallic compounds (IMC) formation along the interfaces and with different morphologies. For instance, ìsunflowerî and ìblockyî faceted shapes have been observed around Ni particle reinforcements incorporated in eutectic Sn-Ag solder matrix. The amount of heat input during the heating stage above the melting temperature of solder has been found to be play a significant role in determining the IMC morphology shape in the Ni particulate reinforced solders. In order to identify and understand the operative mechanisms, similar studies were carried out with Cu and Ag particulate reinforcements in same solder matrix. Solidification and ageing effects are to be discussed. Acknowledgement: Project funded by National Science Foundation under grant No. NSF DMR 0081796.

**4:10 PM Invited**
**Phase Stability and Elastic Properties of Intermetallics Relevant to Electronic Packaging**: *Gautam Ghosh*[1]; [1]Northwestern University, Dept. of Matls. Sci. & Eng., 2225 N. Campus Dr., Evanston, IL 60208-3108 USA

Due to high thermodynamic driving force for interfacial reactions coupled with high mobility of the constituents, intermetallics are formed in solder joints both during fabrication of the devices as well in service.

Depending on the solder chemistry and the metallization scheme, one or more intermetallics may form at the interface. Multicomponent interdiffusion may also cause phase transformation of intermetallic(s). Besides thermodynamic stability of the intermetallics, to understand the processing-structure-property relationship it is important to determine their elastic properties as a first step. Because, in modern electronic packages the intermetallics constitute a significant fraction of the solder joints. We will present the results of a systematic study of the phase stability, elastic properties and fracture toughness of Sn-base intermetallics. The intermetallics considered are $Ag_3Sn$, $AuSn_4$, $Cu_3Sn$, $Cu_6Sn_5$ and $Ni_3Sn_4$. Results include both recent experiments as well as theoretical modeling.

**4:30 PM Invited**

**Interfaces in Lead-Free Soldering and Conductive Adhesive Joining**: *Katsuaki Suganuma*[1]; Keun-Soo Kim[1]; Chi-Won Hwang[1]; Munenori Yamashita[1]; [1]Osaka University, Inst. of Scientific & Industl. Rsrch., Mihogaoka 8-1, Ibaraki, Osaka 567-0047 Japan

Structural integrity of circuits is greatly dependent on interfacial microstructure. In this paper, the current status on various interfaces appearing both in lead-free soldering and in conductive adhesive joining is briefly reviewed. This paper will present the recent data on interfaces in SMT primarily by TEM. Most of Sn alloys involving pure Sn, Sn-Ag, Sn-Bi or their ternary alloys form two intermetallic compounds, Cu6Sn5 and Cu3Sn. The former is much thicker than the latter and their interface integrity is strongly influenced by the Cu6Sn5 layer. The Sn-Zn alloy only forms different intermetallic compounds at the interface with Cu. Plating such as Ni also influences interface integrity. Conductive adhesives, i.e., Ag-epoxy, react with a metal substrate at elevated temperatures. The heat-resistance of the interface is greatly influenced by the presence of Sn plating on a substrate due to the preferential diffusion of Sn to the conductive adhesive layer. From those reaction mechanisms, an ideal interface structure will be discussed.

**4:50 PM**

**Coarsening of the Ternary Eutectic in the Tin-Silver-Copper System**: *Sarah Louise Allen*[1]; Michael R. Notis[1]; Richard R. Chromik[1]; Richard P. Vinci[1]; [1]Lehigh University, Dept. of Matls. Sci. & Eng., Whitaker Lab., 5 E. Packer Ave., Bethlehem, PA 18015 USA

The response of materials used as microelectronics solders to different thermal conditions is of great interest as changes in microstructure, for example coarsening, can have a significant effect on the mechanical properties and hence the reliability of the solder joint. The eutectic tin-silver-copper lead-free solder alloy has been isothermally annealed at a number of different temperatures and at different times in order to ascertain how the ternary eutectic structure coarsens. Cast and directionally solidified alloys at the ternary eutectic composition have been examined by SEM and x-ray mapping to study the changes in microstructure, and quantitative image analysis has been used to obtain the effective activation energy of the coarsening process. It has been observed that the two intermetallic phases present in the eutectic, $Cu_6Sn_5$ and $Ag_3Sn$, coarsen at different rates and both migrate to grain boundaries during the annealing process.

**5:05 PM Invited**

**Effects of Intermetallic Morphology at Metallic Particle/Solder Interface on Dynamic Mechanical Properties of Sn-Ag Solder Joints**: *H. Rhee*[1]; K. C. Chen[2]; J. G. Lee[1]; K. N. Subramanian[1]; [1]Michigan State University, Dept. Cheml. Eng. & Matls. Sci., E. Lansing, MI 48824-1226 USA; [2]California Polytechnic State University, Matls. Eng. Dept., San Luis Obispo, CA 93407 USA

Dynamic thermal/mechanical analysis (DTMA) using a Solids Analyzer and creep tests with a miniature frame were carried out to investigate the effects of morphology of intermetallic compound reinforcements on mechanical properties of Sn-Ag solder joints under simulated service conditions. These intermetallic reinforcements with different morphologies resulted around metallic particles added to the solder depending on reflow profile used. Such particle reinforced composite solders were prepared by mechanically dispersing Cu, Ni or Ag particles into the eutectic Sn-3.5Ag solder paste. The morphology, size and distribution of the intermetallic phases at particulate/solder interface of the solder joints were also characterized metallographically. As a result, a better understanding of the role of the morphology of the reinforcing phases on the mechanical properties of the composite solder joints is obtained. Acknowledgement: Work supported by National Science Foundation under grant NSF DMR-0081796.

## Science and Technology of Magnetic and Electronic Nanostructures: Semiconductor Nanostructures

*Sponsored by:* Electronic, Magnetic & Photonic Materials Division, Jt. EMPMD/SMD-Chemistry & Physics of Materials Committee

*Program Organizers:* Ramamoorthy Ramesh, University of Maryland, Department of Materials and Nuclear Engineering, College Park, MD 20742 USA; Y. Austin Chang, University of Wisconsin-Madison, Department of Materials Science & Engineering, Madison, WI 53706-1595 USA; Robert D. Shull, NIST, Magnetic Materials, Gaithersburg, MD 20899-8552 USA

Tuesday PM Room: 15A
March 4, 2003 Location: San Diego Convention Center

*Session Chair:* Darrell G. Schlom, Pennsylvania State University, Dept. of Matls. Sci. & Eng., University Park, PA 16802 USA

**2:00 PM**

**Effects of Microstructures of Mixed III-V Layers on Electronic and Optical Properties**: *Subhash Mahajan*[1]; [1]Arizona State University, Dept. of Cheml. & Matls. Eng., PO Box 876006, Tempe, AZ 85287-6006 USA

It will be demonstrated that atomic species in mixed III-V layers, residing on the same sub-lattice and differing in their covalent tetrahedral radii, are not randomly distributed within the layers. Two types of deviations from randomness are observed: (1) phase separation, and (2) atomic ordering. Both of these microstructural features evolve at or near surfaces during the layer growth. Phase separation reduces carrier mobility and ordering affects band gap. In addition, it will be shown that the reliability of light emitting devices containing mixed layers is enhanced because non-radiative recombination glide and climb is difficult in the presence of phase separation and ordering.

**2:45 PM**

**Morphological Evolution of Compositionally Modulated Nanowires**: *Timothy D. Sands*[1]; [1]Purdue University, Sch. of Matls. Eng. & Sch. of Electl. & Compu. Eng., MSEE Bldg., Northwestern Ave., W. Lafayette, IN 47907-1289 USA

Whereas equilibrium considerations may present theoretical limits to heterostructure design in thin films, the equilibrium state represents a more practical design limitation for nanowires. The relatively rapid evolution toward local equilibrium in a nanowire heterostructure can be utilized to an engineering advantage in the design of new device materials. In this talk, modeling of local equilibrium states uniquely accessible in the nanowire format is highlighted. In the case of longitudinal lattice-mismatched heterostructures, it will be shown that elastic relaxation normal to the nanowire axis expands the range of lattice-mismatched materials that may be grown coherently in mechanical equilibrium. In a second example, it will be demonstrated that composition modulation along an as-grown nanowire can be used to direct the morphological evolution toward the fabrication of monosized capsules, spheres or periodic constrictions with spatial periods less than the minimum wavelength for Rayleigh breakup.

**3:30 PM**

**Preparation and Properties Nanocrystals and Nanocrystal Superlattices: Building with Artificial Atoms**: *Christopher B. Murray*[1]; [1]IBM Corporation, T. J. Watson Rsrch. Ctr., 1101 Kitchawan Rd., Rte. 134, PO Box 218, Yorktown Heights, NY 10598 USA

Synthetic chemistry allows to production nanometer scale structures which are uniform size to + or - one lattice constant while controlling crystal shape, structure and surface passivation. We combine a high temperature solution phase synthesis with size selective processing techniques to produce organically passivated magnetic and nanocrystals with size distributions less than 5%. These nanocrystals then form the basis for a combined structural and magnetic study of the evolution nanocrystal properties with size. These monodisperse nanocrystals self-organize during controlled evaporation to produce 2D and 3D superlattices (colloidal crystals, opals). The nanocrystals resemble ìartificial atomsî sitting on regular close-packed superlattice sites, each separated by a selected organic spacer. The inter-particle spacing can be varied from intimate contact up to ~40≈ separation. The superlattices retain and enhance many of the desirable mesoscopic properties of individual nanocrystals and permit the first systematic investigation of new collective phenomena. Our goal is to study the properties of both the dispersed nanocrystals and assemblies as all major structural parameters are varied (composition, size, and spacing). Procedures have been developed for Co, Ni, and FePt magnetic nanocrystals as well as for CdSe and PbSe semiconductor quantum dots. Recent explorations of magnetic recording the transport phenomena in magnetic nanocrystal superlattices will be discussed as well as optical studies of the semiconductor nanosctructures. Progress in the development of techniques to pattern nanocrystal superlattices, which will be essential to the fabrication of devices incorporating these molecular-scale building blocks will also be highlighted.

**4:15 PM**
**Metal/Semiconductor Nanowire Nanocontacts**: *Suzanne Mohney*[1]; Ahmad Mohammad[1]; Soham Dey[1]; K. K. Lew[1]; Joan Redwing[1]; Marco Cabassi[1]; Theresa Mayer[2]; [1]Pennsylvania State University, Dept. of Matls. Sci. & Eng., 109 Steidle Bldg., University Park, PA 16802 USA; [2]Pennsylvania State University, Dept. of Electl. Eng., University Park, PA 16802 USA

Semiconductor nanowires (NWs) are presently the focus of intense research owing to their potential for use in both interconnects and nanoelectronic devices. Ohmic contacts to the NWs will be required for many of these devices to realize their full potential. However, the restricted geometry of the nanocontacts can be expected to influence current transport as well as interfacial reactions between the metal and the semiconductor. Our group has recently fabricated reacted metal silicide/Si NWs in porous alumina membranes using electrodeposition for the metal NW segments and vapor-liquid-solid (VLS) growth for the Si segments. In this presentation we will discuss an overview of our fabrication method and the results of an investigation into the structural and electronic properties of these nanostructures.

## Surface Engineering in Materials Science - II: Coatings and Properties

*Sponsored by:* Materials Processing & Manufacturing Division, MPMD-Surface Engineering Committee
*Program Organizers:* Sudipta Seal, University of Central Florida, Advanced Materials Processing and Analysis Center and Mechanical, Materials and Aerospace Engineering, Oviedo, FL 32765-7962 USA; A. Agarwal, Plasma Processes, Inc., Huntsville, AL 25811-1558 USA; Narendra B. Dahotre, University of Tennessee-Knoxville, Department of Materials Science & Engineering, Knoxville, TN 37932 USA; John J. Moore, Colorado School of Mines, Department of Metallurgy and Materials Engineering, Golden, CO 80401 USA; C. Suryanarayana, University of Central Florida, Mechanical, Materials & Aerospace Engineering, Orlando, FL 32816 USA

Tuesday PM — Room: 7A
March 4, 2003 — Location: San Diego Convention Center

*Session Chairs:* C. Suryanarayana, University of Central Florida, Mechl., Orlando, FL 32816 USA; J. DeHosson, University of Groningen, Dept. of Applied Physics, Groningen 9747 AG Netherlands

**2:00 PM Cancelled**
**Reaction Enthalpies as Selection Criteria for Metal Coatings**: *Newton Eng Kin Ooi*[1]; [1]Arizona State University, Dept. of Cheml. & Matls. Eng., Tempe, AZ 85287 USA

**2:20 PM**
**Surface Morphology and Roughness Evaluation of Ni-P-W Coatings**: *Fan-Bean Wu*[1]; Jenq-Gong Duh[1]; [1]National Tsing Hua University, Matls. Sci. & Eng., 429R, 4th Eng. Bldg., Sec. II, Guang-Fu Rd. #101, Hsinchu 300 Taiwan

Surface morphologies of the electroless plated Ni-P and Ni-P-W coatings were investigated by Atomic Force Microscopy (AFM). Both coatings exhibited nodular feature with an averaged nodule size of 2-3 mm. The roughness of the coatings evaluated from the AFM image was highly dependent on the acquisition area. The roughness was as low as 2 nm with a scan area of 0.25 mm2, while 24 nm was determined to be a reliable data under sufficient surveying area wider than 25 mm2. The sine profile was adopted as a model of nodular feature to simulate the roughness calculation. The roughness variation reduced significantly for acquisition region larger than one wavelength. The critical acquisition region of one wavelength, corresponding to twice of a nodule diameter, was then determined for a nodular surface on the electroless plating.

**2:40 PM**
**Tribological Performance of Titanium Carbide & Gr Co-Deposited Thin Films**: *Frank Mark Kustas*[1]; Jennifer Sinchak[2]; Jinhui Zhou[2]; Brajendra Mishra[2]; [1]Engineered Coatings, Inc., PO Box 4702, 15422 Winterleaf Ct., Parker, CO 80134 USA; [2]Colorado School of Mines, Adv. Coating & Surface Eng. Lab., 1500 Illinois, Golden, CO 80401 USA

Thin films of titanium carbide (TiC) and graphite (Gr) were fabricated using unbalanced magnetron co-deposition using either a titanium (Ti) or TiC target with Gr strips. The intent was to fabricate composite films with a ceramic matrix for high hardness and wear resistance and a solid lubricant for low friction. Structural and composition investigations were performed using X-ray diffraction and X-ray photoelectron spectroscopy, respectively. Coating properties, scratch adhesion, cracking from indentation with a diamond indenter, nanohardness, galling resistance, and simulated fretting resistance were measured. Films prepared from targets with more Gr had a larger quantity of carbon (C)-C and C-hydrogen (H) bonding (amorphous (a)-C). Nanohardness measurements showed reduced hardness for films with a higher percentage of the a-C constituent. Cracking resistance appears to be higher for films prepared from the TiC & Gr compared to films deposited from the Ti & Gr target.

**3:00 PM Break**

**3:20 PM**
**Cathodic Deposition of Hydroxyapatite without H2 Evolution**: *Zhongwei Zhao*[1]; [1]Central South University, Col. of Metallurgl. Sci. & Eng., Changsha, Hunan 410083 China

Cathodic electrodeposition is a talent process for preparing hydroxyapatite (HAp) coatings on titanium. But dense and adhesive film can not be obtained by transitional method owing to the fact that vigorously evolution of H2 bubble, a product of the reaction 2H2O+2e=2OH-+H2?™, obstruct the nucleation and growth of calcium phosphate crystal. Commonly, thermal treatment of the product at high temperature is necessary for increasing the strength of bioactive film. When H2O2 is added to the electrolyte, there is no H2 evolution on cathode since the dominating electrochemical reaction changed into H2O2+2e=2OH-. The HAp coatings deposited became dense and adhesive.

**3:40 PM**
**Plasma Assisted Coatings on Porous Materials**: *Sharmila M. Mukhopadhyay*[1]; Pratik Joshi[1]; Saswati Datta[2]; John MacDaniel[2]; [1]Wright State University, Mechl. & Matls. Eng., 3640 Colonel Glen Hwy., Dayton, OH 45435 USA; [2]Procter & Gamble, CETL, West Chester, OH 45069 USA

A five-layer stack of hydrophilic (water absorbent) filter paper was taken as the model porous solid that was made hydrophobic (water repellent) by plasma treatment. Influence of process parameters and monomer chemistry on coating effectiveness and plasma permeation was investigated. Water-drop-absorption time can be used as the initial measure of coating effectiveness. For a quantitative understanding, X-ray Photoelectron Spectroscopy (XPS) was used to analyze the surface chemistry of each surface in the stack and correlated with the water contact angle of that surface. It is clear that by adjusting plasma parameters, it is possible to create a porous film that is hydrophobic on one side and hydrophilic on the other. The precise control of coating penetration into inner layers depends mainly on treatment time and monomer chemistry, rather than on plasma pressure and power. Four types of plasma from different fluorine-containing monomers (TDFO, PDFOA, PFDD and PFMCH) have been compared. All are equally effective in coating the ìexternalî surfaces of the stack, but the extent of permeation of the plasma into the inner layers varies with monomer structure. PDFOA produces more penetrating plasma compared to other molecules.

**4:00 PM**
**Oxidation Behaviors of Fe-Mn-Al Alloys with Electroless Nickel and Aluminizing Coatings**: Jyh-Wei Lee[1]; *Jenq-Gong Duh*[2]; [1]Tung Nan Institute of Technology, Dept. of Mechl. Eng., #152, Sec. 3, Pei-Shen Rd., Taipei County 222 Taiwan; [2]National Tsing Hua University, Dept. of Matls. Sci., Rm. 429, Eng. Bldg. #4, 101, Sec. 2, Kuang-Fu Rd., Hsin-Chu 300 Taiwan

Surface modification is a technique to introduce foreign materials onto the surface of engineering component to improve its service behavior and to increase its lifetime. Aluminization and electroless nickel coating techniques were employed and combined to deposit iron-aluminide, electroless nickel and nickel-aluminide on the surface of Fe-31Mn-5.9Al-0.95C alloy, respectively. Phases and microstructure of individual coating layer were investigated with X-ray diffractometer and electron probe microanalyzer. High temperature oxidation behaviors of coatings were evaluated by the 800°C oxidation test. Owing to the spallation of nickel oxide layer, the oxidation performance of electroless nickel coated alloy was not sufficient. However, weight gains of iron-aluminide and nickel-aluminide coated alloys were very low due to the formation of protective Al2O3 layers on surfaces. It is concluded that the oxidation resistance of Fe-Mn-Al alloy is greatly improved by the iron-aluminide and nickel-aluminide coatings on the surface derived from aluminization and electroless nickel coating combinations.

**4:20 PM**
**Development of Surface Engineered Coatings for Dies Used in Material Processing**: *Dalong Zhong*[1]; Stacey Carrera[1]; Arron Michael Peters[1]; Olympia Salas[1]; Brajendra Mishra[1]; John Moore[1]; [1]Advanced Coatings and Surface Engineering Laboratory, Colorado Sch. of Mines, 1500 Illinois St., Golden, CO 80401 USA

This paper will describe the development of surface engineered coatings for die materials that have applications in glass molding, aluminum pressure die-casting and metal stamping. The design concept involves the development of a ìcoating systemî that has: (a) a ìworking layerî that offers a non-wetting, wear and oxidation resistant surface that interfaces with the material to be formed (i.e., liquid glass or aluminum, solid metal); (b) an intermediate multi-layer or compositionally graded layer that will help minimize the thermal and residual stresses that are generated during the process or shot cycling; and (c) a thin (50-100 nm) adhesion layer that improves the adhesion of the coating system to the die surface (substrate). Finite element modeling (FEM) has been used to identify suitable candidate intermediate layers. In each case, a multi-layer coating architecture has been developed. Glass molding dies and forming tools operate in air at elevated temperatures (e.g. 600-1000∞C), and are subjected to chemically active molten glass and thermal cyclic operations. Similarly, aluminum pressure die casting dies operate typically between 150-6000C in air and need to be non-wetting with molten aluminum, while metal stamping dies need to exhibit low lubricity. This work is directed to identify optimized coating systems for dies used in glass molding, aluminum pressure die casting and metal stamping applications in an effort to improve their performance and reliability. In each case, nanostructured, multi-layer thin films have been deposited using magnetron sputtering, and functionally graded coating architectures have been developed based on these nanocomposite thin films.

## Terence E. Mitchell Symposium on the Magic of Materials: Structures and Properties: Phase Transformations and Defect Dynamics - II & Phase Transformations and Defect Dynamics - III

*Sponsored by:* ASM International: Materials Science Critical Technology Sector, Structural Materials Division, SMD-Mechanical Behavior of Materials-(Jt. ASM-MSCTS)

*Program Organizers:* Amit Misra, Los Alamos National Laboratory, Los Alamos, NM 87545 USA; Harriet Kung, Los Alamos National Laboratory, Materials Science & Technology Division, Los Alamos, NM 87545 USA; Stuart A. Maloy, Los Alamos National Laboratory, Los Alamos, NM 87545 USA; Michael Nastasi, Los Alamos National Laboratory, Los Alamos, NM 87545 USA; Ricardo Schwarz, Los Alamos National Laboratory, Los Alamos, NM 87545 USA

Tuesday PM — Room: 10
March 4, 2003 — Location: San Diego Convention Center

*Session Chairs:* Ricardo Schwarz, Los Alamos National Laboratory, Los Alamos, NM 87545 USA; Ivar Reimanis, Colorado School of Mines, Metallurgl. & Matls. Eng. Dept., Golden, CO 80401 USA

**2:00 PM Invited**
**Dislocation Model of Martensite Transformation**: Steven Celotto[1]; Robert C. Pond[1]; John P. Hirth[2]; [1]University of Liverpool, Brownlow Hill, Liverpool L69 3BX UK; [2]114 Ramsey Canyon Rd., Hereford, AZ 85615 USA

Current understanding of martensitic transformations is based on the phenomenological theory of martensitic crystallography (PTMC). The object of the present work is to develop a defect model of the interface consistent with a diffusionless transformation accompanying its motion. As a necessary step towards this goal we have considered the properties of single arrays of disconnections, and compared their crystallographic attributes with predictions based on the PTMC for identical transformations. In the defect model, the lattice parameters determine the topological properties of disconnections (Burgers vector, b, and step height, h). In turn this determines the disconnection spacing, since these accommodate coherency strains on the terraces, and the habit plane orientation through the defectsí step height. Also components of b perpendicular to the terraces give rise to a rigid body rotation of the crystals away from their reference orientation. Experimental observations obtained using TEM will be shown which corroborate the defect model.

**2:30 PM Invited**
**Martensitic Transformations in Platinum Modified Nickel Aluminide Bond Coats for Thermal Barrier Coatings**: *Kevin J. Hemker*[1]; [1]Johns Hopkins University, Dept. of Mechl. Eng., Baltimore, MD 21218 USA

Thermal barrier coatings used in commercial gas turbine engines insulate the engine components from the hot gas stream. There are four main layers in a thermal barrier system: the superalloy substrate, a nickel aluminide bond coat, a thermally grown oxide (TGO) that grows on the top of the bond coat, and the ceramic top coat. Failure of the TBC is caused by spallation, which is related to the development of stresses and strains in the multi-layered system during thermal cycling. Traditionally, the two main source of stress have been considered to come from: (i) the thermal expansion misfit upon cooling and (ii) the growth of the TGO during service. Recent microstructural observations have highlighted the importance of a martensitic transformation of the bond coat that also plays an important role in governing the underlying properties of the TBC. Results of TEM, micro-probe, X-ray diffraction and microsample tensile testing will be presented and used to characterize the transformation of the bond coat from its original B2 structure to a Ni-rich L10 martensite. The attendant transformation strain and variations in the mechanical properties of the bond coat and will be shown to play an important role in determining the life of the multilayered TBC system.

**3:00 PM Invited**
**Phase Transformations and Phase Stability in the Pu-Ga System**: *Jeremy N. Mitchell*[1]; Marius Stan[2]; Daniel S. Schwartz[1]; Carl J. Boehlert[3]; Thomas G. Zocco[1]; [1]Los Alamos National Laboratory, Nucl. Matls. Tech. Div., MS G721, Los Alamos, NM 87545 USA; [2]Los Alamos National Laboratory, Matls. Sci. & Tech. Div., MS G755, Los Alamos, NM 87545 USA; [3]Alfred University, Dept. of Ceram. Eng. & Matls. Sci., 2 Pine St., Alfred, NY 14802 USA

From room temperature to melting, Pu undergoes five phase transformations that result in a maximum volume change of 20%. The fcc δ phase is stabilized at room temperature by adding small amounts of Ga. Gallium-stabilized δ Pu transforms martensitically to α¥ Pu (monoclinic), but only at low temperatures (~-100∞C). Concurrent to the early work on Pu-Ga in the U.S., Russian scientists developed a phase diagram that shows α Pu + $Pu_3Ga$ stable at room temperature. In this paper, we will present recent experimental results that explore the onset of the δ to α¥ transformation and the thermodynamics of the various phase transformations. We will also present results of phase diagram modeling that incorporate these and previous data. Preliminary results on an internally inconsistent database suggest that α Pu + $Pu_3Ga$ is stable at room temperature thermodynamically, but that the kinetics of the reaction δ Pu to α Pu + $Pu_3Ga$ are extremely sluggish.

**3:30 PM Break**

**4:00 PM Invited**
**Modeling of Amorphization in Network Structures**: *Linn W. Hobbs*[1]; Xianglong Yuan[1]; [1]Massachusetts Institute of Technology, Rm. 13-4054, 77 Massachusetts Ave., Cambridge, MA 02139-4307 USA

The network structures of silicon, silica, silicon nitride and silicon carbide have in common corner-sharing tetrahedra, significant excess volume over close-packed structures, and the requisite structural freedom to be amorphizable by displacive radiation. Topology is important in such tetrahedrally-connected structures and both governs the range of configurations that can be adopted and may be used to characterize them. The principal tool is evaluation of a local unit known as the local cluster based on irreducible ring content. We have used a powerful combination of topology and molecular dynamics simulations to investigate point defect configurations in silicon and silicon carbide, structures of amorphized silicas, and a chemical disorder-driven glass transition in silicon carbide. Some notable findings discussed are that conventional pair-correlations derived from diffraction data cannot distinguish between well-connected silica structures with vastly different topologies, that silicon carbide is amorphizable only above a chemical disorder threshold, and that defects in amorphizing systems can be identified and reliably quantified by topology far after any fiducial reference lattice is lost.

**4:30 PM Invited**
**Nanoscale Probing of Ferroelectric Domain Wall Structure and Dynamics**: *Venkatraman Gopalan*[1]; [1]Pennsylvania State University, Matls. Sci. & Eng., 253 MRL, University Park, PA 16802 USA

This talk will explore the local structure and dynamics of individual domain walls in ferroelectrics. Many new fascinating and unexpected discoveries relating to the presence of wide regions of strain, optical birefringence, and local fields at ferroelectric domain walls were made by Gopalan and Mitchell about 6 years ago. These are forcing us today to revisit our fundamental understanding of the role of atomic defects in ferroelectrics.

**5:00 PM Invited**
**Pressure Effects on Flow, Fracture, and Processing of NiAl**: *John J. Lewandowski*[1]; Robert Margevicius[2]; Joseph D. Rigney[3]; [1]Case Western Reserve University, Dept. Matls. Sci. & Eng., Cleveland, OH 44106 USA; [2]Los Alamos National Laboratory, Los Alamos, NM 87545 USA; [3]GE Aircraft Engines, Evandale, OH USA

The effects of changes in the dislocation substructure on the strength and toughness of stoichiometric polycrystaline NiAl have been determined. The dislocation substructure was introduced via either exposure to high hydrostatic pressure, or via thermomechanical processing by hydrostatic extrusion of polycrystalline NiAl at low temperature. The material tested exhibited a sharp yield point in annealed material. Pressurization removed the yield point without measurably affecting the ductility. Testing with superimposed pressure significantly increased the ductility and changed the fracture mode. Hydrostatic extrusion increased both the strength and toughness due to the beneficial substructure produced. Subsequent annealing experiments were conducted in order to determine the effects of removal of the beneficial dislocation substructure on the resulting strength and toughness.

**5:30 PM**
**Friction Stir Processing for Energy Efficient Surface Modification**: *Glenn J. Grant*[1]; Richard W. Davies[1]; Darrell R. Herling[1]; [1]Pacific Northwest National Laboratory, Matls. Procg. & Performance, 902 Battelle Blvd. P8-35, Richland, WA 99352 USA

Friction Stir Processing (FSP) is a process by which a spinning, non-consumable tool is plunged into a material and translated across the surface, leaving behind a severely plastically deformed region. This is a solid-state process that can be applied to a wide range of materials to potentially improved wear, corrosion, or mechanical properties of the near surface region. FSP also has the potential to modify near surface microstructure or composition to create functionally graded structures, without multiple process steps. Research at the Pacific Northwest National Laboratory has focused on using FSP in two main areas: 1) to create refined grain structures to modify the near surface regions of castings and extrusions for improved microstructure, and 2) to use FSP to stir ceramic particulate into the surface of aluminum alloys to create robust and thick reinforced region for wear applications. The Friction Stir Process has the potential to consume less energy, and produce fewer emissions than many current material processing technologies.

## The Mike Meshii Symposium on Electron Microscopy: Its Role in Materials Research: Iron and Iron Alloys

*Sponsored by:* ASM International: Materials Science Critical Technology Sector, Structural Materials Division, Japan Institute of Metals, SMD-Mechanical Behavior of Materials-(Jt. ASM-MSCTS)
*Program Organizers:* Julia R. Weertman, Northwestern University, Department of Materials Science & Engineering, Evanston, IL 60208 USA; Katherine T. Faber, Northwestern University, Department of Materials Science & Engineering, Evanston, IL 60208 USA; Morris E. Fine, Northwestern University, Department of Materials Science & Engineering, Evanston, IL 60208 USA; Wayne King, Lawrence Livermore National Laboratory, San Ramon, CA 94583-2496 USA; Peter K. Liaw, University of Tennessee, Department of Materials Science and Engineering, Knoxville, TN 37996-2200 USA; Ben Mori, Tokyo 168-0081 Japan

Tuesday PM — Room: 9
March 4, 2003 — Location: San Diego Convention Center

*Session Chairs:* K. Maruyama, Tohoku University, Dept. Matls. Sci., Sendai 980-8579 Japan; C. G. Park, Pohang University of Science & Technology, Ctr. for Adv. Aeros. Matls., Pohang 790-784 Korea

**2:00 PM**
**Structure of a Stress-Induced Martensite Plate and its Formation Stress**: *T. Mori*[1]; Edward Oliver[1]; Mark Daymond[1]; Philip Withers[2]; [1]Rutherford Appleton Laboratory, ISIS Fac., Bldg. R3, Chilton, Didcot OX11 0QX UK; [2]The University of Manchester, Manchester Matls. Sci. Ctr., Manchester M13 9PL UK

A twinned martensite is usually assumed to form with a structure containing fixed fractions of two Bain Correspondence Variants, such that the elastic energy vanishes. Contrary to this assumption, the present work demonstrates that the structure and, consequently, the average transformation strain of a martensite plate depends on external and internal stress. The total energy, consisting of chemical energy, elastic energy and the potential energy of external stress, is minimized under the conditions of constant external stress and temperature. The minimum condition gives the stress required to form the corresponding macroscopic strain due to transformation. The face-centered cubic to face-centered tetragonal transformation in Fe-Pd is used to demonstrate the method. It is shown that the external stress required to initiate martensitic transformation is lower than that predicted using the fixed structure assumption.

**2:20 PM**
**HVEM Observation of Microstructures in Fe-Mn-Si Based Shape Memory Alloys After High Speed Deformation**: *A. Sato*[1]; H. Oonishi[1]; Y. Yamaguchi[1]; S. Kumai[1]; T. Maruyama[2]; H. Kubo[3]; [1]Tokyo Institute of Technology, Dept. of Matls. Sci. & Eng., 4259 Nagatsuta, Midori-ku, Yokohama 226-8502 Japan; [2]Awaji-Sangyo Company, Ltd., M&C Bldg., 2-3-13 Kanda-ogawa-cho, Chiyoda-ku, Tokyo 101-0052 Japan; [3]Kantoh Polytechnic College, 612-1 Mitake, Yokokura Oyama-shi, Tochigi-ken 323-0810 Japan

Fe-Mn-Si based shape memory alloys deformed by a super high-speed roller were examined by HVEM after various heat treatments and mechanical tests. It has been revealed that the strong iron-based shape memory alloy can be rolled down to 50% in thickness reduction by use of Cu plates covering a foil specimen. Microstructures of as rolled and annealed specimens were examined with special interest in the refinement of crystal structure. Application of a 2-1/2 D method enabled us to visualize microscopic distribution of sub-grains and distribution of misorientations that play an important role in strengthening of these alloys. Effects of introduction of second phase particles on the strengthening has also been studied for the purpose of improving the shape memory property by structural refinement.

**2:40 PM**
**Thermography of Fatigue Damage**: *Bing Yang*[1]; Peter K. Liaw[1]; Hsin Wang[2]; Liang Jiang[1]; Jiunn Yuan Huang[3]; Roang Ching Kuo[3]; J. G. Huang[4]; Doug Fieldon[1]; [1]University of Tennessee-Knoxville, Dept. of Matls. Sci. & Eng., Knoxville, TN 37996-2200 USA; [2]Oak Ridge National Laboratory, Oak Ridge, TN 37831 USA; [3]Institute of Nuclear Energy Research (INER), PO Box 3-14, 1000 Wenhua Rd., Chiaan Village, Lungtan 325 Taiwan; [4]Taiwan Power Company, Nucl. Oper. Dept., Taipei 100 Taiwan

An infrared (IR) thermography technique, as a nondestructive evaluation technique, was applied to investigate the fatigue damage of Reactor Pressure Vessel (RPV) Steels during 0.5 Hz, 20 Hz and 1,000 Hz fatigue testing. Five stages of temperature profiles were observed: an initial decrease of the average specimen temperature, a followed temperature hump, an equilibrium temperature region, an abrupt increase of the temperature, and a drop of temperature following specimen failure. The relationship among the temperature and fatigue behavior is discussed. Both thermodynamics and heat-transfer theories are applied to model the observed temperature variation during fatigue. The predicted and measured temperature evolutions during fatigue were found to be in good agreement. Both close from-solution and finite-element methods have been attempted to predict the temperature evolution along the specimen gage-length. The shear-band evolution of the plate specimen during fatigue has been observed and analyzed by thermography.

**3:00 PM**
**Phase Instability and Corrosion of Alloy 22 as a High-Level Nuclear Waste Container Material**: *Yi-Ming Pan*[1]; Darrell S. Dunn[1]; Gustavo A. Cragnolino[1]; [1]Southwest Research Institute, Center for Nuclear Waste Regulatory Analyses(CNWRA), 6220 Culebra Rd., San Antonio, TX 78238 USA

Alloy 22 is currently proposed by the U.S. Department of Energy (DOE) for use as the outer container of the waste package for the disposal of high-level nuclear waste. DOE will need to address the extent to which phase instability resulting from fabrication processes (i.e., welding and postweld treatments) could limit the lifetime of the Alloy 22 waste packages. In this context, recent work involved the study of alloy specimens in mill-annealed condition after thermal exposure at 870°C [1,598°F] for periods of up to 30 minutes. The effect of metallurgical stability on localized corrosion susceptibility was evaluated using corrosion tests and analytical electron microscopy measurements. Results obtained from this study indicate that thermal exposure at 870°C [1,598°F] for only 5 minutes resulted in the formation of topologically close-packed (TCP) phases at grain boundaries; however, no significant alloy depletion was detected in the matrix adjacent to the precipitates nor in the grain-boundary regions between precipitates. Nevertheless, precipitation of TCP phases was found to promote localized corrosion along grain boundaries and decrease repassivation potential in chloride-containing solutions. This abstract is an independent product of the CNWRA and does not necessarily reflect the views or regulatory position of the U.S. Nuclear Regulatory Commission.

**3:20 PM**
**TEM Investigation of Deformation Mechanism of Iron Processed by Severe Plastic Deformation**: *B. Q. Han*[1]; W. A. Chiou[1]; F. A. Mohamed[1]; E. J. Lavernia[1]; [1]University of California-Irvine, Dept. of Cheml. Eng. & Matls. Sci., Irvine, CA 92697-2575 USA

To understand the deformation mechanisms of nanostructured materials, the investigation of grain refinement of pure Fe was performed via severe plastic deformation (equal-channel angular pressing) at room temperature. The microstructural evolution during pressing and the deformation behavior pure Fe were investigated by transmission electron microscopy, and tensile and compressive tests, respectively. The initial grain size of annealed Fe was about 200 mm. It reduced dramatically during pressing and down to about 200-400 nm after 8 passes. In the tension test, a drop in the stress-strain curve following the occurrence of maximum strength was observed in processed Fe, which is different from strain hardening in annealed Fe. In compression test, an initial strain-hardening region followed by a no strain-hardening region was observed in ultrafine grained Fe. The strengthening mechanisms and work-softening behavior were discussed with the evolution of dislocations.

**3:40 PM**
**The Use of EELS Elemental Mapping to Study Small Precipitates in Steels**: Xinyi Y. Wang[1]; *Michael L. Jenkins*[1]; John M. Titchmarsh[1]; [1]University of Oxford, Dept. of Matls., Parks Rd., Oxford OX1 3PH UK

The precipitation processes in an age-hardenable maraging steel with composition 12-Cr-9Ni-4Mo-2Cu (wt%) have been investigated using energy-filtered transmission electron microscopy and conventional high-resolution imaging and diffraction techniques. It proved possible to use EELS elemental mapping to identify and obtain information on the composition of precipitates as small as 1.5 nm. A number of different precipitate types were identified, including Cu-rich precipitates with the bcc and 9R structures, $\omega$-$Fe_7Mo_2$ and $\eta$-$Ni_3$(Ti, Mo), and the formation sequences of these precipitates during ageing were clarified. Ni-rich precipitates tended to form adjacent to existing Cu-rich precipitates, consistent with an earlier suggestion that Cu-rich precipitates act as nucleation sites for $Ni_3$(Ti, Mo) precipitates. The ability of EELS elemental mapping to image Cu-rich precipitates at sizes where they are coherent with the matrix and difficult to image using conventional methods is an important factor in our ongoing investigations of embrittlement of ferritic steels under irradiation.

**4:00 PM**
**Interaction of Coherent Nanoscale Precipitates with Screw Dislocations to Lower the Peierls Stress in Low Carbon Steels**: *Morris E. Fine*[1]; Anthony Tongen[2]; Michael S. Gagliano[3]; [1]Northwestern University, Dept. of Matls. Sci. & Eng., 2225 N. Campus Dr., Evanston, IL 60208 USA; [2]Trinity International University, Dept. of Math./Compu. Info. Sys., 2065 Half Day Rd., Deerfield, IL 60015 USA; [3]Ondeo-Nalco, Metall., One Ondeo-Nalco Ctr., Naperville, IL 60563 USA

Several years ago Mike Meshii was interested in solid solution softening that occurs in iron and certain other metals at certain temperature and strain rate ranges. The screw dislocations in iron and other body-centered cubic metals have a high Peierls stress. Solute atoms were thought to interact with screw dislocations to locally lower the Peierls stress making it easier for them to escape the Peierls valley and produce softening. This concept was based on an early paper by Hans Weertman. Recently a low carbon steel with nanoscale precipitates was found to have a remarkably high Charpy impact fracture energy at cryogenic temperatures. The nanoscale precipitates are thought to interact with screw dislocations reducing the Peierls stress. The present paper applies some of the theoretical treatments developed to explain solid solution softening to the interaction of misfitting coherent nanoscale precipitates with screw dislocations. The activation energy for plastic flow by screw dislocations is reduced. The effects of such interactions on the flow stress-temperature-strain rate relations and the ductile to brittle transformation temperature will be discussed.

**4:20 PM**
**Characterisation of Stress Corrosion Cracks in Stainless Steels and Nickel-Based Alloys**: Sergio Lozano-Perez[1]; *Michael L. Jenkins*[1]; John M. Titchmarsh[1]; [1]University of Oxford, Dept. of Matls., Parks Rd., Oxford OX1 3PH UK

The potential application of TEM for studying the morphology and chemistry of intergranular stress corrosion cracks in components fabricated from stainless steels and nickel-base alloys has been limited by difficulties in sample preparation. We have developed a novel focussed ion beam method, which has proven to be ideal for preparing cross sectional TEM specimens through such cracks. Individual cracks can be pre-selected following characterisation of the crack geometry and grain misorientation by SEM and EBSD, and the site from which the specimen is taken can be chosen with a precision of nanometres. Detailed and novel observations of the microstructure and chemistry of crack flanks and tips will be described which provide new insight into mechanisms of intergranular stress corrosion cracking.

**4:40 PM**
**TEM Studies of Non-Equilibrium Microstructure Evolution and Phase Transformation of Fe-Cr-B-Ni-Mo Spray Coatings**: *H. W. Jin*[1]; C. G. Park[1]; M. C. Kim[2]; [1]Pohang University of Science & Technology, Ctr. for Adv. Aeros. Matls., Dept. Matls. Sci. & Eng., Pohang 790-784 Korea; [2]Research Institute of Industrial Science and Technology, Pohang 790-600 Korea

The non-equilibrium microstructure evolution has been investigated by using TEM in thermally sprayed Fe-Cr-B-Ni-Mo coatings. The spray coated layer was composed of $(Cr,Fe)_2B$ boride particles and $\alpha$-(Fe,Cr) matrix phase containing equiaxed nanocrystallites. The dissolution of $(Cr,Fe)_2B$ followed by the super-saturation of boron within the matrix, during the thermal spraying, could result in a brick-wall type matrix structure through the homogeneous volume nucleation of nanocrystalline $\alpha$-(Fe,Cr) inside the sprayed splats. Thermal stability of these metastable phases and consequent microstructure development have also been investigated by in-situ TEM heating experiments. The sequences of thermal decomposition of the nanocrystalline matrix phase, upon exposure to high temperatures above 670K, to the final intragranular precipitation of $Cr_2B$ borides within the coarsened $\alpha$-(Fe,Cr) grains will be presented.

**5:00 PM**
**Music, Materials, and Metaphysics: Novel Applications of Transmission Electron Microscopy**: *L. E. Murr*[1]; [1]University of Texas at El Paso, Metallurgl. & Matls. Eng., 500 W. University Ave., El Paso, TX 79968-0520 USA

This paper summarizes a number of interesting and often related case studies. Nearly twenty years ago on a Caribbean cruise I vowed to find out how Caribbean steel drums create their chromatic tones. I was convinced that some intricate dislocation structures were involved. Five years ago my students and I cut notes out of steel drums and thinned them down for transmission electron microscope (TEM) examination. Some interesting examples of that work will be presented. In a study of defects in copper rod and very fine wires drawn from the rod, observations of what we called void lobed defects created by copper mist in the wire casting process drew the ire of the industry. Some interesting techniques for observing defect structures in 15-20 µm diameter wires by TEM are illustrated. Recent observations of dynamic recrystallization and associated microstructures in a range of high strain/high-strain-rate phenomena such as friction-stir welded metals and metal shaped charges provide some common processing mechanisms. Some interesting defects were observed in lattice imaging of shock consolidated $YBa_2Cu_3O_7$ superconducting monoliths some years ago and these defects in the {100} planes resemble the Pepsi-ColaÆ logo. Finally, recent efforts to collect nanoparticles in the air suggest considerable potential for respiratory health effects and demonstrate rather interesting microstructural issues about this ultra-fine particle regime.

## The MPMD Fourth Global Innovations Symposium: Energy Efficient Manufacturing Processes: Innovative Sheet Forming and Net-Shape Processing

*Sponsored by:* Materials Processing and Manufacturing Division,
*Program Organizers:* Toni G. Marechaux, National Research Council, National Materials Advisory Board, Washington, DC 20418 USA; Iver E. Anderson, Iowa State University, Ames Laboratory, Ames, IA 50011-3020 USA; Chris Cockrill, DOE Seattle Regional Office, Seattle, WA USA

Tuesday PM — Room: 5A
March 4, 2003 — Location: San Diego Convention Center

*Session Chairs:* Glenn Daehn, Ohio State University, Columbus, OH 43210 USA; Mark T. Smith, Pacific Northwest National Laboratory, Matls. Sci. & Eng., Richland, WA 99352 USA

**2:00 PM Welcome**

**2:05 PM Invited**
**Electromagnetically Assisted Stamping**: *Glenn S. Daehn*[1]; Jianhui Shang[1]; Vincent J. Vohnout[1]; [1]Ohio State University, Matls. Sci. & Eng., 2041 College Rd., Columbus, OH 43210 USA

Electromagnetic forming is a technique where a capacitor is charged to a voltage on the order of a few thousand volts and this energy is run through an acutator near a conductive workpiece. The rapidly changing current in the coil induces a rapidly changing magnetic field that induces eddy currents in the workpiece. In the end a significant repulsion between the workpiece and coil can be attained. Actuators of this type can be embedded in traditional stamping dies. This can produce many advantageous features. In particular strain can be produced exactly where it is needed in a part, giving the process designer unprecidented freedom. This has the practical advantages of 1) enabling the production of part shapes with high strength materials that may otherwise be impossible, 2) fewer press operations may be required to make a given part, and 3) it may be possible to completely eliminate the use of lubricants from the stamping plants. All three of these advantages have significant positive environmental and energy payoffs.

**2:30 PM**
**Inverse Analysis of Aluminum Tubes Hydroformed Under Free Conditions and Within a Conical Die**: *Ba Nghiep Nguyen*[1]; Kenneth I. Johnson[1]; Glenn J. Grant[1]; Mohammad A. Khaleel[1]; [1]Pacific Northwest National Laboratory, Richland, WA 99352 USA

In order to reduce the very costly trial-and-error practices, numerical methods predicting how the material can deform, and the hydroforming parameters are essential. This paper presents an inverse approach to tube hydroforming to efficiently predict the thickness, strain and pressure distributions for a given deformed configuration of aluminum AA6061-T4 tubes under free hydroforming conditions or within a conical die. The analysis employs a membrane finite element formulation within the framework of the deformation theory of plasticity and Hillís criterion to describe the plastic flow. Experiments on hydroforming of Aluminum tubes using a conical die or under free hydroforming conditions were also conducted to validate the model. Good comparisons of results have been found for the deformed configurations in which the bending effect is small.

**2:55 PM**
**A Comparison of Tube-Hydroforming Experiments and Model Results Using a Numerical Process Control Method**: *K. I. Johnson*[1]; B. N. Nguyen[1]; G. J. Grant[1]; M. A. Khaleel[1]; [1]Pacific Northwest National Laboratory, PO Box 999, Richland, WA 99352

The incorporation of process control logic within finite element simulations has the potential to speed the introduction of lightweight materials, such as hydroformed aluminum tubing, into automotive structures. This paper compares the deformations and strains observed in tube-hydroforming experiments with companion finite element simulations that were used to predict the optimum load paths for maximum tube deformations without wrinkling. The tests were conducted using extruded AA-6061-T4 tubes that were formed in both a conical die shape and in a free-hydroforming configuration. A numerical process control method was incorporated in the finite element simulation to predict the increments in the axial end-feed and internal pressure loads to give a constant ratio of axial-to-hoop plastic strain based on a controlled increment in the maximum equivalent plastic strain. The process controller uses the deformation theory to describe the plastic flow and the forming limit diagram to predict the onset of rupture. The end-feed and pressure loads predicted by the models were applied in the tests, and the resulting strains, deformations, and loads to failure were measured for comparison with the model predictions. The hydroforming tests show that the controller accurately predicted the end-feed and pressure load paths that gave stable deformations to the onset of wrinkling in the tube. The finite element model also gave reasonably accurate predictions of the deformed shapes and thinning that were observed in the experiments.

**3:20 PM Break**

**3:40 PM Invited**
**Design of Magnetic Pulse Welding Processes**: *R. Douglas Everhart*[1]; [1]Advanced Computational and Engineering Services, LLC, 13603 Fernlace Ct., Pickerington, OH 43147 USA

Magnetic pulse welding is an impact welding technique that is solid-state in nature. It consists of accelerating a work-piece up to a high velocity (typically 300 to 1200 meters/second) using a magnetic pulse. The high-velocity work-piece strikes a stationary work-piece and a metallurgical impact bond is formed. The process is identical to explosive welding (which has been used for decades) with the exception that the metal is driven with a magnetic pulse, rather than explosives. Design of a quality magnetic pulse welding process involves the consideration of several factors and is a multi-step endeavor. The design goal defines the desired impact conditions (high-velocity work-piece speed and attitude) to produce a quality weld. The characteristics of the magnetic pulse power supply have a strong influence on the welding process. Coil durability (and therefore replacement) is the number one factor for considering the economic advantage of this process over another. Finally, the work-piece tooling and set-up must be designed.

**4:05 PM Invited**
**Clean and Efficient Metal and Powder Forming Through Magnetic Pressing Technology**: *Duane Charles Newman*[1]; [1]IAP Research, Inc., 2763 Culver Ave., Dayton, OH 45429 USA

This paper will address the use of magnetic pressing technology to form metals and produce net shape component from powders. Magnetic pressing refers to a suit of processes that includes electromagnetic forming, Dynamic Magnetic Compaction (DMC) and magnetic pulse welding. The paper describes several applications of the magnetic pressing technology and discusses details of high volume production systems developed by IAP. The benefits of using magnetic pressing technology and their impact on energy efficiency will be highlighted.

**4:30 PM Invited**
**Energy Efficient Production of Sheet Material Using Radiant Arc-Lamp Heating**: *Evan K. Ohriner*[1]; John Rivard[1]; Craig A. Blue[1]; Adrian Sabau[1]; [1]Oak Ridge National Laboratory, Metals & Ceram. Div., PO Box 2008, MS 6083, Oak Ridge, TN 37831-6083 USA

Radiant arc-lamp heating offers the potential for direct production of melted sheet products and foil. A focussed 300 kW arc lamp provides incident radiant heat at a flux of up to 3 kW/ cm2. The melting of sheet materials of metals, intermetallic alloys and composite materials has been achieved. The process offers the advantages of: 1) high efficiency of conversion of electrical energy to absorbed incident energy, 2) the ability to transmit radiant energy through a quartz window enabling environmental isolation of processed material, and 3) processing of large areas of material at rates of the order of 10 cm2/s. Current research efforts include control of grain structure and texture in the solidified sheet and numerical modeling of melting and solidification sheet materials.

## Universities Servicing Education, Research and Technology Internationally for the Aluminium and Light Metals Industries - I

*Sponsored by:* Light Metals Division, LMD-Aluminum Committee
*Program Organizer:* Subodh K. Das, Secat, Inc., Coldstream Research Campus, Lexington, KY 40511 USA

Tuesday PM — Room: 5B
March 4, 2003 — Location: San Diego Convention Center

*Session Chairs:* Sara Dillich, US Department of Energy, Office of Industl. Tech., Washington, DC 20585-0121 USA; Subodh K. Das, Secat Inc., Coldstream Rsrch. Campus, Lexington, KY 40511 USA

**2:00 PM**
**Measurements of Bubble Dispersion and Other Bubble Parameters in a Gas Fluxing Unit at Alcoa Using a Capacitance Probe**: *James W. Evans*[1]; Neeta Mittal[1]; Autumn Fjeld[1]; D. Corleen Chesonis[2]; [1]University of California, Matls. Sci. & Eng., Berkeley, CA 94720 USA; [2]Alcoa Inc., Alcoa Techl. Ctr., Alcoa, PA 15069 USA

A capacitance probe has been developed at Berkeley that is intended to measure the frequency with which bubbles pass a point in liquid aluminum. The probe is comprised of an inner conducting wire (in some cases two wires) that is separated from the liquid aluminum by an alumina sheath. It works by detecting the change in capacitance, between the wire and the aluminum, which occurs when the aluminum moves back from the sheath as a bubble passes. Because only alumina is in contact with the melt, the probe is robust and can survive several hours in the metal. The software necessary for processing the signals from the probe is described. The probe has been used to measure bubbles in a fluxing unit at the Alcoa Technical Center and the difficulties in doing so are described. Results are presented and their relevance to modeling and optimization of fluxing units discussed. Research cofunded by DOE Energy Efficiency and Renewable Energy.

**2:20 PM**
**Surface Behavior of Aluminum Alloys Deformed Under Various Processing Conditions**: *Wojciech Z. Misiolek*[1]; William H. Van Geertruyden[1]; Paul T. Wang[2]; [1]Lehigh University, Inst. for Metal Forming, 5 E. Packer Ave., Bethlehem, PA 18015 USA; [2]Alcoa Technical Center, Process Tech. Div., 100 Techl. Dr., Alcoa Ctr., PA 15069 USA

The fundamentals of surface defect formation in extruded and rolled 6xxx aluminum alloys are not yet completely understood. These defects include peripheral coarse grain (PCG) structure, spangled surfaces, surface tearing, heat checking and pick-up. The objective of this paper is to understand the origins and mechanisms of the formation of surface imperfections for peripheral coarse grain (PCG) structure as the first step to understand surface behavior of aluminum alloys deformed under various processing conditions. This paper will include results of compression, rolling, and laboratory scale extrusion tests, in which deformation parameters are closely controlled. The deformed material is characterized to understand the influence of processing conditions and alloy chemistry on surface defect formation using traditional metallography and electron backscatter diffraction techniques. The goal is to use the results to generate a material response model that can predict these imperfections and help prevent their occurrence.

**2:40 PM**
**Microstructure and Texture Evolution of Continuous Cast and Direct Chill Cast AA 5052 Aluminum Alloy During Annealing**: *Jiantao Liu*[1]; *Xiangming Cheng*[2]; Tongguang Zhai[1]; James G. Morris[1]; [1]University of Kentucky, Dept. of Cheml. & Matls. Eng., 177 Anderson Hall, Lexington, KY 40506-0046 USA; [2]SECAT, Inc., 1505 Bull Lea Rd., Lexington, KY 40511 USA

In an effort to understand the differences in recrystallization behavior between continuous cast (CC) and direct chill (DC) cast aluminum alloys that potentially lead to differences in formability, investigation was performed on the recrystallization microstructures and textures of industrially produced hot bands of CC and DC cast AA 5052 aluminum alloy (Al-2.4%Mg) during subsequent annealing procedures. Macrotextures, determined by X-ray diffraction pole figures, were analyzed using three-dimensional orientation distribution functions (ODFs). The electron backscatter diffraction (EBSD) technique was adopted to study microtextures and mesotextures. The effects of annealing temperature, annealing time and cold rolling reduction on texture evolution during annealing process were studied. Both microstructures and textures during annealing are compared between the CC and DC materials.

**3:00 PM**
**Reduction of Annealing Times: Development of a Model for Recrystallization in Hot Deformed Aluminum**: *Anthony D. Rollett*[1]; Mohammed H. Alvi[1]; Hasso Weiland[2]; Jaakko Suni[2]; [1]Carnegie Mellon University, Matls. Sci. & Eng., 5000 Forbes Ave., Wean Hall 4315, Pittsburgh, PA 15213 USA; [2]Alcoa Inc., Alcoa Techl. Ctr., 100 Techl. Dr., Alcoa Ctr., PA 15069 USA

The kinetics of recrystallization are being studied with respect to crystallographic orientation (texture) in hot deformed aluminum. Two alloys, 1005 and 5005 and included in the study which is aimed at reducing annealing times for the processing of aluminum alloy sheet and plate. Results will be described for the kinetics and microstructural characteristics of recrystallization after hot deformation. When coupled with conventional methods such as hardness measurement, use of automated electron back-scatter diffraction (EBSD) in the scanning electron microscope (SEM) affords a powerful tool for quantifying the variation in behavior as a function of orientation. Results will be described from annealing of as hot-rolled plate, and material subjected to hot deformation under a variety of temperatures and strain rates.

**3:20 PM**
**Development of Integrated Methodology for Thermomechanical Processing of Aluminum Alloys**: *Ben Q. Li*[1]; David Field[1]; [1]Washington State University, Sch. of Mechl. & Matls. Eng., Sloan 207, Pullman, WA 99164 USA

This seminar discusses a research project on the development of a finite element-based integrated mechanical and microstructural model for process understanding and design sensitivity analyses for thermomechanical processing of aluminum alloys and the validation of the integrated model through bench-mark experiments. The research effort is being carried out in collaboration with researchers at Alcoa. We have made significant progress since it started last August. In essence, a finite element model has been developed, which has incorporated both the total formulation and rate formulation for large nonlinear deformation associated with thermomechanical processing of aluminum alloys. The finite element model development is based on our in-house finite element code, which will provide flexibilities required to integrate with complex constitutive relations describing the microstructure development during large deformation processes. Numerical simulations have been carried out for single crystal plasticity and poly-grain crystal plasticity for aluminum alloys. Channel die experiments have been carried out with aim to develop a reliable constitutive relation that describes the microstructure evolution during plastic deformation and to validate the finite element-based model predictions. Modeling strategies, numerical simulations and experimental measurements as well as the comparison of numerical results and experiments will be presented.

**3:40 PM Break**

**3:50 PM**
**Microstructural Processes Occurring During Hot Deformation of AA 7055**: *Blythe E. Gore*[1]; Henry A. Padilla[2]; Ian M. Robertson[1]; Armand J. Beaudoin[2]; Jonathan A. Dantzig[2]; Hasso Weiland[3]; [1]University of Illinois at Urbana-Champaign, Matls. Sci. & Eng., 1304 W. Green St., MC-246, Urbana, IL 61801 USA; [2]University of Illinois at Urbana-Champaign, Mechl. & Industl. Eng., 1206 W. Green St., MC-244, Urbana, IL 61801 USA; [3]Alcoa Inc., Alcoa Techl. Ctr., 100 Technical Dr., Alcoa Ctr., PA 15069 USA

In hot working of 7xxx series aluminum alloys, the thermomechanical processing window is limited by problems such as hot shortness and by property requirements such as fatigue and fracture toughness. Industrial rolling conditions are such that stress must be sustained near the melting point of secondary phases, thus making it necessary to understand the underlying precipitation and deformation mechanisms involved to predict material response during processing. Evolution of precipitates and microstructural changes during high temperature in-situ TEM deformation have been studied and interactions of dislocations with grain boundaries and particles have been observed. By correlation of these findings with mechanical properties, a material description for hot deformation of AA 7055 has been formulated. This information is being used to develop a two-phase constitutive model for hot deformation processes.

**4:10 PM**
**Process Systems Tools for Design and Optimization of Carbothermic Reduction Processes**: *Dimitrios I. Gerogiorgis*[1]; B. Erik Ydstie[1]; Marshall Bruno[2]; Kai Johansen[3]; [1]Carnegie Mellon University, Dept. of Cheml. Eng., 5000 Forbes Ave., Pittsburgh, PA 15213 USA; [2]Alcoa Inc., Next Generation Al. Processes, Alcoa Techl. Ctr., 100 Techl. Dr., Alcoa Ctr., PA 15069-0001 USA; [3]Elkem ASA Research, PO Box 8040 Vaagsbygd, Kristiansand, N-4602 Norway

Carbothermic reduction is a nontraditional alternative process 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 operation 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 the direct chemical reduction pathway. This method is identified as a potential alternative to Hall-HÈroult electrochemical reduction by several studies, but its complexity still poses remarkable technical obstacles for implementation. Interdisciplinary collaboration is crucial in combining academic and industrial expertise: thus, a collaborative team has been formed among Carnegie Mellon University, ALCOA and ELKEM, in order to create an integrated modeling environment for design, control and economic analy-

TUESDAY PM

sis. It is important to underline that this systematic process development procedure is the standard in the petrochemical industry. Nevertheless, it is much less followed in the metallurgical industry, because of its traditional nature and the complexity of high-temperature metallurgical processes. The philosophy of this collaboration is to advance the carbothermic program more efficiently by introducing the use of Process Systems Engineering theory and Computer Aided Design tools. The main advantage of the systems approach to conceptual design is that process alternatives can be rapidly evaluated for economic feasibility at little cost, using detailed computer simulations. The availability of models and tools in a CAD environment thus allows us to speed up design. Furthermore, a sensitivity analysis can evaluate the importance of uncertain process parameters and provide sound guidelines for efficient experiment design, thus economizing on expenditure. Thermodynamics, kinetics, computational fluid dynamics, thermophysical material properties, large scale numerical solution and optimization strategies and economic evaluation methods are all facets of our modeling in order to evaluate the feasibility of various reactor configurations. The strategic goal here is to design a modeling environment for design of carbothermic reactors: A number of complementary objectives need to be pursued to advance towards this major goal: the creation of a framework for information storage, modeling, design and economic analysis, the development of steady state and dynamic, total (ODE) and distributed (PDE) process models, the efficient integration of commercial process simulation tools with physical property databases and the identification of sensitive variables (useful for pilot plant design and experiment design) are some of these objectives that can drastically expedite development, reducing costs and time. Presently distributed and newly acquired knowledge from ongoing work must also be integrated into a common modeling framework for rapid evaluation, optimization and experiment design.

**4:30 PM**
**Aluminum Electrorefining in Ionic Liquids via Near Room Temperature Electrolysis**: *Venkat Kamavaram*[1]; Ramana G. Reddy[2]; [1]The University of Alabama, Dept. of Metallurgl. & Matls. Eng., A129 Bevill Bldg., Tuscaloosa, AL 35487-0202 USA; [2]The University of Alabama, Dept. of Metallurgl. & Matls. Eng. & Ctr. for Green Mfg., 27th Ave., A129 Bevill Bldg., Tuscaloosa, AL 35487-0202 USA

Electrorefining of aluminum alloys in ionic liquids via near room temperature electrolysis was investigated. The applicability of different ionic liquids such as 1-methyl-3-butylimidazolium chloride ($C_4$mimCl) + $AlCl_3$ and 1-methyl-3-hexylimidazolium chloride ($C_6$mimCl) + $AlCl_3$ in the electrorefining process was studied. In the present study, electrorefining of two different alloys Al-356 and Al-360 alloy was performed. The effect of experimental parameters such as cell voltage, concentration of the electrolyte and temperature was studied for both the electrolytes. The physicochemical properties such as viscosities, densities, decomposition temperatures and electrochemical windows of these electrolytes were determined. The electrorefining process has the advantages of low energy consumption, low temperature and no pollutant emissions compared to the current industrial processes.

**4:50 PM**
**A Network for Aluminum Research**: *Rung Tien Bui*[1]; [1]Universite du Quebec a Chicoutimi, NSERC-ALCAN Industl. Rsrch. Chair in Proc. Eng., Chicoutimi, Quebec G7H 2B1 Canada

REGAL, a province-wide network of Quebec institutions of higher learning, R&D agencies and technology users has been set up to carry out research in aluminum fabrication and transformation technologies, and to help channel the expertises and the resources into large projects with more efficiency in terms of generating synergy and fundings, cutting-edge research, qualified personnel training, and technology transfers. This paper aims at presenting this unique experience in collaborative, mutipartite, university-based R&D. In addition to discussing the research program, the paper covers topics like dispersed inter-institutional collaboration and management, resources sharing, search for new fundings, joint graduate training, intellectual properties. Examples are drawn from activities conducted jointly with major aluminum industries worldwide.

## Yazawa International Symposium on Metallurgical and Materials Processing: Principles and Technologies: Slags and Fluxes

*Sponsored by:* Extraction & Processing Division, EPD-Process Fundamentals Committee, EPD-Pyrometallurgy Committee, EPD-Aqueous Processing Committee, EPD-Copper, Nickel, Cobalt Committee, EPD-Lead and Zinc Committee, Jt. MPMD/EPD-Process Modeling Analysis & Control Committee: See Plenary Session for Co-Sponsors

*Program Organizers:* Hong Yong Sohn, University of Utah, Department of Metallurgical Engineering, Salt Lake City, UT 84112-0114 USA; Kimio Itagaki, Tohoku University, Institute for Advanced Materials, Sendai 980-8577 Japan; Florian Kongoli, FLOGEN Technologies, Inc., Materials Technology Department, Montreal, Quebec H3S 2CS Canada; Chikabumi Yamauchi, Nagoya University, Department of Materials Science & Engineering, Nagoya 464 8603 Japan

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| Tuesday PM | Room: Solana |
| March 4, 2003 | Location: San Diego Marriott Hotel |

*Session Chairs:* Kazuki Morita, The University of Tokyo, Dept. Metall., Tokyo 113-8656 Japan; Florian Kongoli, FLOGEN Technologies Inc., Matls. Tech. Dept., Montreal, Quebec H3S 2C3 Canada

**2:30 PM Keynote**
**Slags and Fluxes in Pyrometallurgical Processes**: *Florian Kongoli*[1]; [1]FLOGEN Technologies, Inc., Matls. Tech. Dept., 5757 Decelles Ave., Ste. 511, Montreal, Quebec H3S 2C3 Canada

Slags and fluxes are important interexchanged dimensions of pyrometallurgical processes. They can increase the efficiency of the smelting, converting and refining processes and improve the quality of the final products. A good slag, in one hand, should have appropriate physicochemical properties such as low liquidus temperature, optimal viscosity, maximum ability to attract undesirable elements, minimum potential of attracting valuable elements, etc. A good flux, on the other hand, when properly used, can considerably improve the physicochemical properties of the slag since by modifying its chemical composition it can decrease the liquidus temperature, improve viscosity etc. Consequently, the choice of a good slag and the corresponding fluxing strategy has become indispensable in most of industrial processes. However, the properties of multicomponent slags as well as the effect of several fluxes used in practice today are known only empirically. Sometimes they have been globally asserted without taking into account the characteristics of individual processes, the positioning of the initial slag composition or the particularities of certain laboratory procedures used to assert these effects. In the todayís reality of frequent changes in the composition of the raw materials and that of the fluxes themselves, in the existing or new developing technologies, the quantification of the physicochemical properties of the multicomponent slags and the effect of fluxes becomes indispensable. This paper reviews the work carried out from the authorís group during the last 15 years on the quantification of the physicochemical properties of multicomponent slags and on the effect of fluxes in several smelting and converting processes in close relation to individual characteristics of these processes. Several examples have also been given in order to demonstrate the fact that when taken outside the context some fluxes can become in fact anti-fluxes.

**3:05 PM**
**Phase Diagram of CaO-FeOx-Cu2O Slag Under Copper Saturation**: *Yoichi Takeda*[1]; [1]Iwate University, Fac. of Eng., Ueda 4-3-5, Morioka 020-8551 Japan

The CaO-FeOx-Cu2O slag system has been practically applied to continuous converting of copper, and also has potential for refining of copper. Liquidus lines of the slag system under copper saturation and phase stability diagram for the existing compounds are presented. Slag and copper metal were melted in a magnesia crucible. Liquidus composition was determined by chemical analysis of slag sample saturated solid phase. The temperatures of invariant equilibria were investigated by thermal analyses. Oxygen potentials on the liqudus lines, the univariant and invariant equilibria were extrapolated from the relation between slag composition and oxygen potential, that relation was confirmed in separate experimental work.

**3:30 PM Invited**

**Some Aspects of Calcium Ferrite Slags**: *Sharif Jahanshahi*[1]; [1]CSIRO Minerals, Clayton, Saint-Petersburg, Victoria 3168 Australia

Calcium ferrite slags are often associated with Professor Yazawa due to his pioneering work on thermodynamics of this type of melts. Over the past years CSIRO has invested some effort in studying physico-chemical properties of such melts to fill in some of the gaps in our knowledge and explore opportunities for application of the understanding developed. These investigations cover thermodynamics, transport properties of calcium ferrite based slags as well as the kinetics of reactions of such slags with gases or refractories. The present paper provides an overview of some of these studies and highlights some of the interesting behavior of such melts.

**4:00 PM**

**A Counter-Flow Batch Process for Refining Copper Using Sodium Carbonate Slags**: *Hiroshi Hashimoto*[1]; Mitsuru Tanahashi[1]; Hong Yong Sohn[2]; Chikabumi Yamauchi[3]; Kunihiko Takeda[1]; [1]Nagoya University, Dept. of Matls. Sci. & Eng., Grad. Sch. of Eng., Furo-cho, Chikusa-ku, Nagoya, Aichi 464-8603 Japan; [2]University of Utah, Dept. of Metallurgl. Eng., 135 S. 1460 E., Rm. 412, Salt Lake City, UT 84112-0114 USA; [3]Chubu University, Dept. of Mechl. Eng., Sch. of Eng., 1200 Matsumoto-cho, Kasugai, Aichi 487-8501 Japan

For the application of sodium carbonate slag treatment to product high purity copper on an industrial scale, the counter-flow batch operation, which can reduce the amount of utilized slag, was proposed from a viewpoint of a post-treatment of slag. Based on the distribution ratios of several impurities between the slag and molten copper determined previously, the effectiveness of this operation is discussed using a mathematical model and confirmed experimentally. According to the model, the slag consumption to remove Sb to a required level in case of the counter-flow batch operation is calculated to be around 30% of that in case of a ordinary batch operation, where pure sodium carbonate is used as a slag at every stage.

**4:25 PM Break**

**4:35 PM Invited**

**Dissolution Mechanism and Solubility of Chlorine in the Oxide Melts**: *Kazuki Morita*[1]; Taro Hirosumim[1]; Makoto Miwa[1]; [1]The University of Tokyo, Dept. Metall., 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656 Japan

Ecological problems have recently been treated in iron- and steel-making processes, as is seen in the development of waste plastic injection into a blast furnace in Japan. However, we have to develop more effective and more extensive utilization of such a high temperature mass production system for the waste management. At present, waste plastic containing chlorine such as polyvinyl chloride (PVC) cannot be treated due to the problem of dioxine and HCl generation as well as the erosion of refractories. In order to develop the waste treatment system for the materials containing chlorine, its behavior in high temperature furnaces must be predicted and the evaluation of chlorine gas absorption into slags becomes essential, which is also very important for the practical incineration process. However, no data are available regarding the thermodynamic properties of chlorine in molten slags, because it has not been treated as impurities in molten iron such as S, P and N. In the present study, thermodynamic properties of chlorine in the $CaO-SiO_2-Al_2O_3$, $Na_2O-SiO_2-Al_2O_3$, $CaO-SiO_2-Al_2O_3-Na_2O$, $CaO-SiO_2-FeO$ and $CaO-SiO_2-Al_2O_3-FeO$ slags have been investigated in the present study. The experiments were carried out using gas-slag equilibrium, controlling both $PO_2$ and $PCl_2$ simultaneously ($PO_2=10^{-6}$-$10^{-19}$ atm, $PCl_2=10^{-6}$-$10^{-13}$ atm at 1673-1748K), and the solubility of chlorine in the 40mass%CaO-40mass%$SiO_2$-20mass%$Al_2O_3$ slag was found to vary in proportion to $PO_2^{-1/4}$ and $PCl_2^{1/2}$. Accordingly, the chloride capacity ($C_{Cl-}$), which represents the ability of slags to absorb chlorine, has been defined; The $C_{Cl-}$ values were observed to increase with increasing slag basicity and temperature, and showed a reasonable relationship with that of $C_{S^{2-}}$.

**5:05 PM Invited**

**Selection of Slag Composition and Structure for Autogenous Smelting Process to Produce White Metal Using the Basic Developments of Prof. A. Yazawa**: *V. M. Paretsky*[1]; A. V. Tarasov[1]; [1]State Research Center of Russian Federation, State Rsrch. Inst. of Non-Ferrous Metals ìGintsvetmetî, 13 Acad. Korolyov St., Moscow 129515 Russia

The basic work conducted by Prof. A. Yazawa has demonstrated that in order to ensure single-stage white metal production by autogenous smelting of copper sulfide raw materials, it is most favorable to use highly basic slags, in particular oxide systems CaO-FeO-Fe2O3-SiO2. The main advantage of this system is its homogeneity at normal smelting temperatures (1200-1400∞C) and within the common ranges of calcium-to-iron ratios under high partial oxygen pressures. Ferrite-calcite slags proposed by Prof. A. Yazawa and his followers found practical use for the first time in the well-known Mitsubishi process. In order to provide a more rigorous substantiation of the selection of the slag composition for the autogenous smelting to produce white metal, special studies have been conducted in the Gintsvetmet Institute to investigate the composition and structure of slags produced on a semi-commercial scale when testing the KFP and FBP processes for white metal smelting, as well as the slag obtained in a full-scale KFP furnace at the Almalyk copper smelter. These studies were conducted using mineralogical microscopy techniques, a Cameca microprobe and nuclear gamma-resonance (NGR) spectroscopy. Studies were carried out using solidified and quenched slags with different cooling rates: 103∞C/sec (bar sample) and $10^6$∞C/sec (superfast quenching by spinning-disc method). In the latter case, the structure of liquid slag was preserved (super-cooled liquid) permitting more definite assessment of the true structure of slag in molten state. The NGR-spectra obtained have indicated that: ∑ bar sample (quenching rate of $10^3$∞C/sec) characterizes an intermediate state between liquid and solidified slag (60% fyalite and 40% vitreous phase); ∑ two types of positions occupied by Fe2+ ions have been identified: tetrahedral (A-positions) and octahedral (B-positions); it should be pointed out that Fe2+ ions occupy preferably positions in octahedral vacancies, while Ca2+ ions occupy only octahedral vacancies and Si4+ ions only tetrahedral vacancies; ∑ with an increase in the Ca2+/Fe2+ ratio the proportion of Fe2+ ions in A-positions increases and that in B-positions decreases resulting in a lower probability of replacement of Fe2+ ions with Cu2+ ions which are located only in B-positions; ∑ an increase in the SiO2 concentration in slag results in occupation of A-positions with Si4+ ions leaving vacant B-positions for Fe2+ ions, and as a consequence, increasing the probability of copper dissolution in slag; ∑ the total proportion of Fe2+ ions in molten slag increases with a higher concentration of CaO in slag. The investigations conducted have demonstrated why production of high-grade matte or white metal is associated with lower loss of copper in slag in a series: silicate slag/silicate-calcium slag/ferrite-calcium slag.

**5:35 PM Invited**

**Ferrous Calcium Silicate Slags in Direct to Blister Flash Smelting**: *Asmo Vartiainen*[1]; Ilkka V. Kojo[2]; Cesar AcuÒa Rojas[3]; [1]Outokumpu Research Oy, Pori 28101 Finland; [2]Outokumpu Technology, Espoo 02201 Finland; [3]Codelco, Chuquicamata Chile

Background of Direct-to-Blister Flash Smelting is discussed; especially slag chemistry relating to copper solubility, slag fluidity and impurity behavior. In December, 2000, Mini-pilot Flash Smelting test runs were carried out at Outokumpu Research Oy to produce blister copper from Chilean concentrate and white metal and from a mixture of them. Tested slag types were iron silicate slag, ferrous calcium silicate slag and calcium ferrite slag with different slag compositions and different concentrate/white metal ratios. The test runs were successful. The fluxing effect of copper oxide was clearly demonstrated and ferrous calcium silicate slags remained fluid on a very wide liquidus range. The distribution of arsenic between ferrous calcium silicate slag and blister copper is much higher than between iron silicate slag and blister copper. This successful test run with the new slag type offer new possibilities in Direct-to-Blister process design.

## Yazawa International Symposium on Metallurgical and Materials Processing: Principles and Technologies: Advances in Non-Ferrous Production Technologies and Industrial Practice: Copper I

*Sponsored by:* Extraction & Processing Division, EPD-Process Fundamentals Committee, EPD-Pyrometallurgy Committee, EPD-Aqueous Processing Committee, EPD-Copper, Nickel, Cobalt Committee, EPD-Lead and Zinc Committee, Jt. MPMD/EPD-Process Modeling Analysis & Control Committee: See Plenary Session for Co-Sponsors

*Program Organizers:* Hong Yong Sohn, University of Utah, Department of Metallurgical Engineering, Salt Lake City, UT 84112-0114 USA; Kimio Itagaki, Tohoku University, Institute for Advanced Materials, Sendai 980-8577 Japan; Florian Kongoli, FLOGEN Technologies, Inc., Materials Technology Department, Montreal, Quebec H3S 2CS Canada; Chikabumi Yamauchi, Nagoya University, Department of Materials Science & Engineering, Nagoya 464 8603 Japan

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| Tuesday PM | Room: Santa Rosa |
| March 4, 2003 | Location: San Diego Marriott Hotel |

*Session Chairs:* Ron M. Sweetin, Mitsubishi Materials Corporation, Oakville, Ontario L6J 4B2 Canada; Mineo Hayashi, PT. Smelting, Gresik E. Java 61151 Indonesia; Motoo Goto, Port Kembla Copper Pty. Ltd., Port Kembla, NSW 2505 Australia

**2:30 PM Keynote**

**Recent Advances in Modern Continuous Converting**: *Motoo Goto*[1]; *Mineo Hayashi*[2]; [1]Port Kembla Copper Pty., Ltd., Military Rd., Port Kembla, NSW 2505 Australia; [2]PT. Smelting, Desa Roomo, Kecamatan Manyar, Gresik, E. Java 61151 Indonesia

Today, Pierce-Smith converters, coupled together with various types of smelting units, are used in most of the worldís smelters. However, due to the ìbatchî processing nature, and problems associated with fugitive emissions during the transfer of melt and blowing stages, this arrangement will unlikely be adopted in future smelters. Modern day alternative processes include the Mitsubishi Process, Outokumpu Flash Smelting and Flash Converting Process, the Noranda Process, and the Ausmelt Process, but only the Mitsubishi Process is a ìtruly continuousî smelting and converting operation, producing a constant flow of blister without tapping, and is economically proven by long term commercial operations. This paper reviews recent advances in modern continuous converting technologies, with a special section devoted to operation of the ìfirst standalone Mitsubishi C-furnaceî coupled together with a Noranda Reactor, at Port Kembla Copper Pty. Ltd. in Australia.

**3:00 PM**

**Development of New Copper Continuous Converter**: *Yasuo Ojima*[1]; *Yasuhiro Kondo*[1]; *Kazunori Kawanaka*[1]; Keisuke Yamamoto[1]; [1]Sumitomo Metal Mining Company, Ltd., Niihama Rsrch. Labs., 17-5 Isoura-cho, Otu 145-1 Funaya Saijo, Niihama, Ehime 792-0002 Japan

New copper continuous converting process was investigated to evaluate the possibility to be applied for the commercial operation. The tests were performed with scaling up from the laboratories crucible experiments to the pilot plant test. Bath smelting process with using top submerged lance technology was applied in these tests. Furnace shape was modified to the lengthwise cylindrical shaped one with having the settling area. The furnace monitor was put in the settling area to check inside furnace. FeOx-SiO2, FeOx-CaO and FeOx-CaO-SiO2 based slag system were used for this test to check their efficiency. The optimum slag chemistry to have good metallurgical results in this pilot test was discussed and FeOx-CaO system with adding some SiO2 was turned out to be preferable, which has not been practically used. In this pilot plant test feeding rate of 1 t/H of solid grain matte was charged consecutively for two weeks and continuous converting could be done successively. This process is supported to overcome the problems of existing processes and be easily applied for existing plants.

**3:25 PM Invited**

**New Approach for the Optimization of Copper Concentrates Flash Combustion by the Control of Blends**: *Roberto Parra*[1]; Roberto Parada[2]; Marcelo RodrÌguez[1]; [1]Universidad de ConcepciÛn, Dept. of Metallurgl. Eng., Edmundo Larenas 270, ConcepciÛn Chile; [2]CompaÒÌa Minera Disputada de Las Condes, Chagres Smelter, Pedro de Valdivia 291, Santiago Chile

The classic criteria in the preparation of the charge for the smelting of copper concentrates in a flash furnace consider the mass and energy balance from the chemical and mineralogy composition of the concentrates. The operation parameters fixed with this method donít assure the stability of the operation and critical problems of slag quality and dust formation occur very often. This paper present the results of a laboratory test that allows the prediction of the behavior of concentrates blends in view to the minimization of dust formation and magnetite control in the slag. The combustion of different copper concentrates and blends were done in a drop tube furnace. The results show that the magnetite and dust formation donít have a linear behavior with the weight proportion of the blend and some optimal blends of 2 or 3 types of concentrates can be identified. From the reasonable hypothesis that the qualitative behavior of blends in the drop tube represents the real behavior in the burner, the preparation of the charge with this approach could help to solve those operational problems.

**3:50 PM**

**Effect of Magnetic Field on the Rate of Slag Reduction in an Electric Furnace**: *Victor Montenegro*[1]; Andrzej Warczok[1]; Tashiharu Fujisawa[2]; Gabriel Riveros[1]; [1]Universidad de Chile, Av. Tupper 2069, Santiago 2777 Chile; [2]Research Center for Advanced Waste and Emission Management, Furo-Cho, Chikusa-ku, Nagoya 464-8603 Japan

Smelting of copper concentrate in Teniente Converter produces highly oxidized slag, containing from 4 to 10% Cu and from 15 to 25% of Fe3O4. Copper recovery requires magnetite reduction to a level of 5%, determining the degree of cuprous oxide co-reduction and liberation of copper matte inclusions. Rate of slag reduction is controlled by the mass transfer to the reaction interface. Slag stirring affects the rate of reduction and enhances coalescence of mechanically entrained copper matte inclusions. Slag reduction and sedimentation in AC electric furnace is commonly used method of slag cleaning. Utilization of DC electric furnace creates beneficial conditions introducing slag electrolysis on top of chemical reductions with carbon of coke and electrodes. Application of external magnetic field, interacting with direct current in an electric furnace, induces magnetohydrodynamic phenomena, such as intensive stirring and electromagnetic buoyancy force acting on inclusions. Laboratory scale research in simulated DC electric furnace with superimposed magnetic field, show a significant acceleration of the rate of slag reduction and copper removal. Continuous measurement of gas flow and composition allowed for determination of the reduction rate along the time. Application of external magnetic field in reduction of industrial slag in a crucible simulated DC electric furnace results in the increase of reduction rate from 7 to 15 times, comparing with the identical conditions in AC electric furnace. Interaction of non-homogeneous electric field with crossed permanent magnetic field induces vigorous slag stirring enhancing mass transfer and accelerating the rate of slag reduction. Additional participation of slag electrolysis in magnetite and cuprous oxide reduction as well as acceleration of inclusions settling by electromagnetic buoyancy force affect in slag cleaning intensification.

**4:15 PM Break**

**4:25 PM Invited**

**Ausmelt Technology, Flexible, Low Cost Technology for Copper Production in the 21st Century**: *Joseph Sofra*[1]; Robert Matusewicz[1]; [1]Ausmelt, Ltd., 12 Kitchen Rd., Dandenong, Melbourne, Victoria 3175 Australia

It has become increasingly evident that sustainable metals production in the 21st century requires producers to balance the needs of cost effective, high value production with that of responsible plant operation. This is becoming more difficult as lower grade and more complex feed materials, including recycled scrap and residues, are being processed to reduce production costs and decrease exposure to primary metal market fluctuations. One particular facet of the metals industry facing these challenges in the 21st century are copper producers. The recent steady decline in the copper price has seen the industry cut expenditure, tighten control on income streams and focus on high returns on capital investment. For these reasons copper producers are looking towards flexible technologies that can deliver high value products, with minimal environmental impact at low capital and low sustainable operating costs. Ausmeltís Top Submerged Lancing (TSL) technology for copper production is a low cost, proven technology for the processing of both primary and secondary copper materials. Both the smelting and converting operations introduce significant advantages in environmental performance, improved process efficiencies and high rates of metal recovery. Ausmelt has made significant gains in the past 4 years in establishing a strong market position for its copper technology. New installations in China, South Africa and India as well as existing operations in Zimbabwe and China have demonstrated its effectiveness. This paper reviews the application of Ausmelt Technology for both smelting and converting of primary and secondary sources. It discusses Ausmeltís design and implementation philosophy, and how this philosophy meshes with the needs of the end user.

**4:50 PM**

**Quantification of the Liquidus Surface of ìLime Ferriteî Slags at Several Oxygen Potentials**: *Florian Kongoli*[1]; Ian McBow[1]; Akira Yazawa[2]; [1]FLOGEN Technologies, Inc., Matls. Tech. Dept., 5757 Decelles, Ste. 511, Montreal, Quebec H3S 2C3 Canada; [2]Tohoku University, 16-32, Niizaka, Aoba-ku, Sendai 981 Japan

ìLime ferriteî slag with limited silica content has proven to be a valuable choice in the modern processes of copper smelting and converting due to several advantages that this slag offers compared to the classical silicate slags. Nevertheless the liquidus surface of this slag has been experimentally measured only at low oxygen potentials such as in equilibrium with iron or near it and in air. Although most of the smelting and converting processes that use this slag occur at intermediate oxygen potentials, the liquidus surface of this slag is not known at these conditions and the effect of oxygen potential and silica has not been correctly understood. This has brought some confusion in literature as well as in the industrial practice. In this work the liquidus surface of the lime ferrite slags has been quantified by the means of a new thermophysicochemical model and a new type of liquidus surface diagrams which is very convenient for any industrial process that uses lime ferrite slags. These diagrams ca n be easily used to select the lowest liquidus temperature of lime ferrite slags at a minimum cost and can help design several fluxing strategies in copper smelting and converting processes. The effect of the oxygen potential, silica and copper is also quantified and important industrially related conclusions are drawn.

**5:15 PM**

**Direct Copper Production by Cyclone Smelting**: *I. Wilkomirsky*[1]; R. Parra[1]; [1]University of ConcepciÛn, Dept. of Metallurgl. Eng., Edmundo Larenas 270, ConcepciÛn 270 Chile

The conventional classical production of blister considers the oxidation of sulfur and iron from copper concentrates in two consecutive steps, although there are no physicochemical reasons why blister copper can not be produced in a single stage. The practical limitations are related to the technology that determines the thermal conditions and the kinetics in different reactors. An analysis was done to determine the conditions required for a cyclonic reactor pilot plant to produce blister copper directly from concentrates. The best metallurgical results were obtained with the cyclonic reactor operating at above 1450∞C.

**5:40 PM Invited**

**The Chilean Copper Metallurgical Industry: An Update**: *A. Valenzuela*[1]; J. Palacios[2]; D. Cordero[3]; M. S·nchez[4]; [1]Chilean Copper Comission, Santiago Chile; [2]University of Atacama, CopiapÛ Chile; [3]CODELCO, El Teniente Div., Rancagua Chile; [4]University of ConcepciÛn, ConcepciÛn 270 Chile

In the last years, Chile continue being the top producer of copper, either in the form of concentrates or electrowinning and electrorefining cathodes, the last one obtained from seven smelters, which have carried out several modernization plans either to increase smelting capacity or to achieve environmental regulations established in the Chilean legislation. This paper updates the current situation of the Chilean copper metallurgical industry developed in the last years, regarding technological innovations in smelters, environmental regulations and presenting solutions for management of SO2, particulate matter and arsenic, considering that Chile is the worldís largest copper producer. Also, the authors emphasize the important role played by CODELCO Chile, the more important state owner copper company, developing Chilean technologies, as El Teniente Converter and El Teniente Slag Cleaning Furnace.



## Yazawa International Symposium on Metallurgical and Materials Processing: Principles and Technologies: Aqueous and Electrochemical Processing III

*Sponsored by:* Extraction & Processing Division, EPD-Process Fundamentals Committee, EPD-Pyrometallurgy Committee, EPD-Aqueous Processing Committee, EPD-Copper, Nickel, Cobalt Committee, EPD-Lead and Zinc Committee, Jt. MPMD/EPD-Process Modeling Analysis & Control Committee: See Plenary Session for Co-Sponsors

*Program Organizers:* Hong Yong Sohn, University of Utah, Department of Metallurgical Engineering, Salt Lake City, UT 84112-0114 USA; Kimio Itagaki, Tohoku University, Institute for Advanced Materials, Sendai 980-8577 Japan; Florian Kongoli, FLOGEN Technologies, Inc., Materials Technology Department, Montreal, Quebec H3S 2CS Canada; Chikabumi Yamauchi, Nagoya University, Department of Materials Science & Engineering, Nagoya 464 8603 Japan

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| Tuesday PM | Room: Pacific |
| March 4, 2003 | Location: San Diego Marriott Hotel |

*Session Chairs:* Adam C. Powell, IV, Massachusetts Institute of Technology, Dept. of Matl. Sci. & Eng., Cambridge, MA 02139-4301 USA; Ryosuke O. Suzuki, Kyoto University, Dept. of Energy Sci. & Tech., Kyoto, 606-8501 Japan

**2:30 PM Invited**

**OS ProcessñThermochemical Approach to Reduce Titanium Oxide in the Molten CaCl2**: *Ryosuke O. Suzuki*[1]; Katsutoshi Ono[1]; [1]Kyoto University, Dept. of Energy Sci. & Tech., Yoshida-Honmachi, Sakyo-ku, Kyoto 606-8501 Japan

A new cell concept for calciothermic reduction is presented where titanium dioxide is used as the raw material for reduction. It bases on the thermochemical requirement that metallic calcium is needed as the reductant, CaCl2 as the solvent. The thermodynamic phase equilibria and physical properties are analyzed to optimize the reaction and to separate the product. The reduction system consists in a single cell, where both the reduction reaction and the electrolytic reaction for recovery of reducing agent coexist in the same molten calcium chloride bath. TiO2 powder is directly top-charged into themolten CaCl2. A few %Ca dissolves in the melt, and it constitutes the media with a strong reducing power. TiO2 + 2 Ca+ + 2 e- = Ti + 2 Ca2+ + 2 O2- Sufficiently deoxidized titanium metal deposits agglomerate rapidly and form granular sponge, which sink down to the bottom of the cell. Both mechanisms of the halide flux deoxidation and the electrochemical deoxidation work efficiently for these fine precipitates. The reducing agent is in situ recovered by electrolysis of CaO, which is supplied as the by-product of reduction. The molten CaCl2 has a relatively large solubility for CaO. At the anode: C + 2 O2- = CO2 + 4 e- At the cathode: Ca2+ + e- = Ca+ Some cell designs and modifications are proposed for industrial applications.

**3:00 PM**

**Preparation of Uniform Ultra-Fine Nickel Oxalate Particles by Chelating Precipitation**: Huang Kai[1]; Chen Huiguang[1]; [1]Central South University, Sch. of Metallurgl. Sci. & Eng., Lushannanlu, Changsha, Hunan 410083 China

Uniform spherical and fiber-like nickel oxalate particles were prepared by chelating precipitation method, which is by adding the oxalate acid into the solution of ammine nickel chloride. The reactive concentration of the ammine nickel chloride and the oxalate acid are the key factors to the morphologies of the final particles, i.e., low reactive concentrations(<0.1 mol) of the two reagents are in favor of the formation of fiber-like particles while high reactive concentrations are in favor of the formation of spherical particles. The feeding methods and the agitation strength all have effects on the particle formation, which experimentally proved the above formation mechanism to be reasonable.

**3:25 PM**

**Anion-Exchange Separation in HCl Media for the Ultra-High Purification of Cobalt**: *Tamas Kekesi*[1]; Masahito Uchikoshi[2]; Kouji Mimura[3]; Minoru Isshiki[3]; [1]University of Miskolc, Miskolc, Egyetemvaros 3515 Hungary; [2]Fine Materials Corporation, Tagajo 985-0843 Japan; [3]Tohoku University, Inst. for Adv. Matls. Procg., Sendai 980-8577 Japan

Anion exchange in HCl media is considered an efficient alternative to the combination of the conventional purification methods. Anion-exchange distribution functions have been determined for cobalt and the main impurity elements by the technique of batch equilibration. Results were confirmed by spectrophotometric investigations and elution tests. Based on the new and the available distribution functions, combined with the assessment of thermodynamic stability, a procedure of anion exchange separation has been devised to eliminate virtually all the impurities from the cobalt-chloride solution. Separation of copper has been enhanced by the introduction of a preliminary step under reduced conditions. The rest of the impurities are eliminated in a second anion-exchange step applying rinsing and elution stages under oxidized conditions. The optimum parameters of the procedure have been determined according to performance characteristics (purification ratios, yields and volume efficiencies) derived from the analysis of elution curves obtained with laboratory scale ion-exchange columns. Special computer programs have been developed to facilitate thermodynamic simulation, analytical correction and data processing.

**3:50 PM**

**Morphological Characteristics of Nickel Particles Electrodeposited from Aqueous Solution**: *Guo Xueyi*[1]; Zhang Chuanfu[2]; Zhang Duomo[2]; Masazumi Okido[3]; Huang Kai[2]; Li Qihou[2]; [1]The University of Tokyo, Ctr. for Collaborative Rsrch., Komaba 4-6-1, Meguro-Ku, Tokyo 153-8505 Japan; [2]Central South University, Col. of Metallurgl. Sci. & Eng., Changsha, Hunan 410083 China; [3]Nagoya University, Ctr. for Integrated Rsrch. in Sci. & Eng., Furo-cho, Chikusa-ku, Nagoya 464-8603 Japan

In this study, the electrolytic nickel powder was deposited from the NiSO4-NH4Cl-NaCl-H3BO3-H2O solution. The morphological characteristics of the nickel particles electrodeposited from this aqueous solution were investigated. The effects of the electrolyte constituents, the parameters for the electro-deposition on the morphology of the nickel particles were addressed. It is concluded that not only the particle size, but also the morphology of the deposited nickel particles strongly depend on the electrolyte constituents and technical conditions. Especially, it is observed that the growth of the particle morphology is strongly related to the duration for electro-deposition. The ultra-fine nickel particles with flake, nodular or dendrite shape may be easily deposited by just controlling the time interval for particle growth. Further, the influences of various conditions on the particle morphology were explained, the growth mechanism of the particle electro-deposited from the solution was elucidated.

**4:15 PM Break**

**4:25 PM Invited**

**Detailed Mathematical Modeling of Liquid Metal Streamer Formation and Breakup**: David Dussault[1]; *Adam C. Powell*[1]; [1]Massachusetts Institute of Technology, Dept. of Matl. Sci. & Eng., 77 Massachusetts Ave., Rm. 4-117, Cambridge, MA 02139-4301 USA

A three-dimensional Cahn-Hilliard phase field model is formulated to describe transport-limited electrochemical reactions coupled with fluid flow in a metal reduction cell. When the reaction is limited by mass transfer of metal ions from the electrolyte to the cathode, the metal-electrolyte interface at the cathode exhibits a Mullins-Sekerka instability, leading to the growth of dendrite-like ìstreamersî of liquid metal into the electrolyte, which in turn significantly enhance the apparent mass transfer coefficient there. Model results for iron reduction from ferrous oxide in slag show formation of these streamers, and their breakup due to the instability of the cylindrical liquid-liquid interface. Although the double-layer is not included in this model, the related phenomenon of electrocapillarity is represented by a gradient penalty term which includes the electric potential gradient, such that interfacial energy is a function of the electric field normal to the interface.

**4:55 PM Invited**

**Purification of Leach Solutions by Direct Solvent Extraction**: *Chu Yong Cheng*[1]; Mark Urbani[1]; [1]AJ Parker Cooperative Research Centre for Hydrometallurgy/CSIRO Minerals, Australia, Conlon St, Waterford, PO Box 90, Bentley, WA 6982 Australia

The solvent extraction (SX) processes of the four nickel plants in Australia and the Goro SX process in New Caledonia were reviewed. The use of intermediate precipitation, solids/liquid separation and re-leach in the three WA nickel plants and the use of Cyanex 301 for a direct solvent extraction (DSX) process in the Goro process make these processes complicated and costly in capital and operation. The research work carried out by the SX group at the AJ Parker Cooperative Research Centre for Hydrometallurgy/CSIRO Minerals has led to the invention of DSX processes to recover nickel and cobalt from leach solutions. The simplicity of the process flowsheets and the expected savings in capital and operating costs are the major advantages of the new DSX processes over the reviewed processes. By using a new synergistic organic system in semi-continuous tests with a pilot plant leach solution from BHP-Billiton Stainless Steel Materials (after iron precipitation), the metal values (Ni and Co) together with zinc and co pper were separated from the major impurities (Mn, Mg and Ca, together with Cl) in the first SX circuit. The co-extracted manganese, magnesium and calcium were easily scrubbed out. After stripping, the metal values (Ni and Co) together with zinc and copper were concentrated, resulting in a much smaller second SX circuit and equipment in the down stream processes. The extraction and stripping kinetics of the metals with the new synergistic organic solution were very fast. Within 0.5 minutes, the extraction and stripping almost reached steady state. Semi-continuous test work with a synthetic leach solution, a cobalt pilot plant leach solution from Peko Rehabilitation Project Pty Ltd and a synthetic solution to simulate a concentrated solution from BHP-Billiton Stainless Steel Materials showed that manganese, calcium, copper and zinc can be effectively and efficiently separated from nickel, cobalt and magnesium by extraction, scrubbing and stripping. This led to the invention of another type of DSX process using D2EHPA to recover nickel and cobalt from leach solutions.

**5:25 PM**

**Nontoxic Method of Nickel/Cobalt/Copper Sulfides Precipitation as Rich Concentrates from Diluted Sulphate Solutions**: *M. I. Kalashnikova*[1]; Y. M. Shneerson[1]; M. V. Keskinova[1]; V. V. Chetvertakov[1]; [1]Norilsk Nickel RJS, Gipronickel Institute JS, Saint-Petersburg Russia

Results of investigations concerning precipitation of heavy non-ferrous metals from solutions using precipitators based on elemental sulphur and lime with gypsum transfer to a separate product are given.

**5:50 PM**

**The Polymorph Transformations of Antimony White**: Xiao Songwen[1]; Yan Xiaohui[2]; Xiao Xiao[1]; [1]Changsha Research Institute of Mining & Metallurgy, Lushannanlu, Changsha, Hunan 410012 China; [2]Hunan Sunrise Nanometter Material Company, Ltd., Yuwanzheng, Changsha, Hunan 410014 China

On ground of the theoretical models of growth unites with coordination polyhedron structure of anion, the polymorph transformation mechanisms of antimony white Sb2O3 in hydro-process was presented. The new findings had been verified in the commercial-scale test, and it showed that a small amount of tratrate ions in the solution was effective for the crystal transformation of antimony white in hydro-process.

## Yazawa International Symposium on Metallurgical and Materials Processing: Principles and Technologies: Recycling, Waste Treatment and Environmental Issues III

*Sponsored by:* Extraction & Processing Division, EPD-Process Fundamentals Committee, EPD-Pyrometallurgy Committee, EPD-Aqueous Processing Committee, EPD-Copper, Nickel, Cobalt Committee, EPD-Lead and Zinc Committee, Jt. MPMD/EPD-Process Modeling Analysis & Control Committee: See Plenary Session for Co-Sponsors

*Program Organizers:* Hong Yong Sohn, University of Utah, Department of Metallurgical Engineering, Salt Lake City, UT 84112-0114 USA; Kimio Itagaki, Tohoku University, Institute for Advanced Materials, Sendai 980-8577 Japan; Florian Kongoli, FLOGEN Technologies, Inc., Materials Technology Department, Montreal, Quebec H3S 2CS Canada; Chikabumi Yamauchi, Nagoya University, Department of Materials Science & Engineering, Nagoya 464 8603 Japan

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| Tuesday PM | Room: Leucadia |
| March 4, 2003 | Location: San Diego Marriott Hotel |

*Session Chairs:* Douglas Raymond Swinbourne, RMIT University, Sch. of Civil & Cheml. Eng, Melbourne, Victoria 3001 Australia; Venkoba Ramachandran, Ram Consultants, Scottsdale, AZ 85262 USA

**2:30 PM Invited**

**Treatment of Aqueous Effluents for Recovery and/or Removal of Metals in Non-Ferrous Metalsí IndustryñA Review**: *Venkoba Ramachandran*[1]; [1]Ram Consultants, 9650, E. Peregrine Pl., Scottsdale, AZ 85262 USA

In view of the increasing environmental regulations that have been promulgated in the last 30 years, non-ferrous smelters and refineries have learnt to handle effectively the process waste streams that need to be bled from the system for impuritiesí control. The cations of concern are copper, lead, zinc, cadmium, mercury, thallium, nickel, silver, sodium and potassium. Anionic species of arsenic and selenium also need to be addressed. Sulfates and chlorides-not a major problem at present- have come under scrutiny in the recent past. The current paper reviews several treatment options with reference to a)types of waste streams processed b)process chemistry c)discharge options and recovery of treated water and d)sludge disposal. The long term goal of any smelter and/or refinery should be to have zero liquid discharge from the plant. Methods to obtain zero discharge are discussed.

**3:00 PM**

**A Dynamic LCA Model for Assessing the Impact of Lead Free Solder**: *M. A. Reuter*[1]; E. Verhoef[1]; A. Scholte[1]; G. Dijkema[1]; [1]Delft University of Technology, Dept. of Appl. Earth Scis., Mijnbouwstraat 120, Delft 2628 RX The Netherlands

While the importance of LCA to support decision-making, in particular to environmental impact assessment, is widely acknowledged, there is also some criticism. LCAs are very data intensive, which means the success of a study is strongly dependent on the availability of good data. Thus may explain why in many studies time dependence is neglected, and production of materials are considered individually. Although this may give rise to significant errors in calculated environmental impact, because of the interconnectedness and dynamics of systems considered. The carbon cycle, for example, is interlinked both via the non-hydrocarbon components of commercial plastics, such as chlorine and heavy metals, and via residues from refining and coals based operations. The production of one material, therefore, often is interrelated to and dependent on the consumption or generation of another. Most of the raw materials for silver production, for example, are not concentrated silver ores, but obtained as by-products of copper, steel and zinc production. When primary production of these material changes, silver production is affected. Similarly, in case outlets for arsenic cease to exist, primary production of copper, lead and zinc must be modified. Similar to this, the recovery of one material can interrelate to the recovery of another. The recycling of copper from messing or the steel from cars also produces zinc. On that account, a dynamic, hierarchical model of a number of interconnected material cycles is developed. The model includes detailed models of the production and waste management stages to connect production or recovery of one material to the production of others. As the interconnection of metal production occurs at process level, modelling of the different production route involves considering the different types of production processes individually. The model is constructed on the basis of mass balances, in which the lower system levels represent increasing technical detail. Consistent with Reuter (1996) split factors, or recoveries, are used to model the processes. Data reconciliation is used on calculate the split factors from literature values on process feed, products and residue composition to ensure data quality. National, European or world production figures on process capacity can be used to calculate the relative contribution of processes. The model is set up dynamically. The continuous generation of new products, by-products, and material wastes result changes of the production network, e.g. the selection resources or suppliers employed, factory locations, innovation of facilities and products. In the model these changes can be considered, e.g. by changing the distribution of material flows over the different processes, or changing the split factors in time. The hierarchical structure allows matching the information needs of the different actors, supporting and/or coordinating decision-making processes in industry, SWM and governments. Municipal waste flows can be estimated from series of production data and assumption on delay of materials in the consumption phase. This allows for the evaluation of solid waste policy options in different dynamic scenarios with respect to the environment and resource depletion, but also the evaluation of the impact of lead-free soldering. The hierarchical structure allows In addition to the absolute environmental impacts, the model can be used to evaluate relative impact of policy, infrastructure or product design on the whole system as well.

**3:25 PM**

**Disposal Treatment of Alternative CFC Gas(C2H2F4) Using Chemical Reaction with Metal Compounds**: *Hideki Yamamoto*[1]; Akihiro Kushida[1]; Norihiro Murayama[1]; Junji Shibata[1]; [1]Kansai University, Dept. of Cheml. Eng., Fac. of Eng., 3-3-35, Yamatecho, Suitashi, Osaka 564-8680 Japan

A new technology to make alternative CFC gas (C2H2F4:R-134a) used as refrigerant of an air cooling units or a refrigerators convert directly into a harmless substance have been established and new concept on the disposal treatment of global warming gas was presented. Reaction vessel made of Hastroy steel was applied to examine the chemical reaction of R-134a with metal chloride and metal oxides at the valuable experimental conditions. The effect of the kind of metal compound on the chemical reaction activity for the disposal treatment of R134-a gas was examined in this experiment. In the case of metal chloride(CaCl2, MgCl2), the beginning temperature of these chemical reactions are at 700K-770K and the reaction percentage of solid phase base is about 30-60%. Beginning temperature of the chemical reaction with metal oxide(CaO) is 820K, and the reaction percentage of solid phase base is about 60%. Experimental results verify that the chemical reactions can be take place at substantially lower temperature of 700 K-850K as compared with the combustion treatment method(1300K-1500K). Reaction product is mainly metal fluoride which is a harmless and a valuable chemical material as new resource. The other favorable characteristics are that the continuous treatment is possible at a low temperature under atmospheric pressure. Furthermore this process is compact, easily controllable and safely operable at low running cost. This paper concerns with a new harmless disposal treatment of toxic global warming gas.

**3:50 PM**

**Modelling and Control of Dioxin Formation During Iron Ore Sintering**: *Pengfu Tan*[1]; Dieter Neusch¸tz[2]; [1]Portovesme s.r.l., S.P.n.2-Carbonia/Portoscuso, Portoscuso 09010 Italy; [2]Rheinisch-Westf‰lische Technische Hochschule Aachen, Lehrstuhl f¸r Werkstoffchemie, Aachen D-52056 Germany

In order to minimize dioxins and furans formation in iron ore sinter plants and to possibly avoid expensive end-of-pipe removal stages, thermodynamic calculations on the stability of PCDD/Fs have been combined with sinter process modelling by means of kinetic simulations and computational fluid dynamics. Three thermodynamics databases of PCDD/Fs, derived using the Group Additivity approach and two computational molecular modeling methods, MNDO and PM3, respectively, combined with the SGTE database have been used to model the PCDD/F formation and the PCDD/F isomer distributions in iron ore sintering. The results show very similar conditions for the PCDD/F formation using the different databases. The predicted isomer distributions of toxic PCDD/Fs have been compared with measured data from sinter plants, electrical arc furnaces, waste incinerators and wood burning furnaces. The calculated data using the database derived from the MNDO method show the best agreement with the industrial measurements. The thermodynamic calculations also show that the isomer distributions found in combustion processes are equilibrium values, while the concentration ratio of PCDDs and PCDFs in the wind boxes does not represent an equilibrium state. A CFD model of iron ore sintering was developed including the kinetics of 15 relevant chemical reactions with the aim of describing the chemical and the thermal processes of sintering and the gas flow patterns. On the basis of these informations possible pathways for the PCDD/F formation in sinter plants have been identified: Between charging zone and center part of the sinter bed, PCDD/Fs are formed below the hot zone, carried downwards with the gas and condensed in the cold zone. Transported to the discharge end with the solid mixture, they are again released into the gas phase when the flame front approaches the bottom of the bed. In addition, PCDD/Fs are formed in the last wind boxes when the hot offgases cool down and reach the critical temperature range. Consequently, methods to reduce the dioxin formation reactions are proposed including inhibitor addition and off-gas quenching.

**4:15 PM Break**

**4:35 PM Invited**

**Behaviour of Thallium During Direct Lead SmeltingñA Thermodynamic Viewpoint**: *Douglas Raymond Swinbourne*[1]; Akira Yazawa[2]; [1]RMIT University, Sch. of Civil & Cheml. Eng., PO Box 2476V, Melbourne, Victoria 3001 Australia; [2]Tohoku University, 16-32 Niizaka, Sendai 981-0934 Japan

Thallium is a minor element found in lead ores. The behaviour of thallium during lead smelting has become of much more interest recently due to the toxic effect it had on maintenance staff at one particular smelter. In this paper the behaviour of thallium will be examined using computational thermodynamics techniques for the case of direct smelting of lead concentrate by several generic technologies. Such methods have been pioneered by Prof. Yazawa to model many processes in extractive metallurgy. It will be shown that thallium behaviour is strongly influenced by the presence or absence of certain secondary recycle materials in the charge and by the way in which the smelter offgases are handled.

**5:05 PM**
**Environmental Assessment of Imperial Smelting Process Practice in China**: *Guo Xueyi*[1]; Xiao Songwen[2]; Li Qihou[2]; Nie Zuoren[1]; Zhang Duomo[2]; Yamamoto Ryoichi[1]; [1]University of Tokyo, Ctr. for Collaborative Rsrch., Komaba 4-6-1, Meguro-Ku, Tokyo 153-8505 Japan; [2]Central South University, Col. of Metallurgl. Sci. & Eng., Changsha, Hunan 410083 China

Imperial Smelting Process is one of important method to produce Zinc & Lead. Shaoguan Smelter in South China is a representive metallurgical plant to adopt ISP for the zinc and lead production with the annual production capacity of about 200 thousand tons. In this study, by analyzing the resource use, energy consumption and waste emission and disposal, the environmental burden of the ISP practice in this smelter was addressed, the impact assessment was conducted quantatively by applying some environmental indicators, and further the approaches for improving the resource & energy use efficiency as well as releasing the environmental burden were proposed.

**5:30 PM**
**Use of Solid Hematite to Fix Arsenic Contained in a Gas Phase**: *A. Gonzalez*[1]; E. Balladares[1]; R. Parra[1]; M. S·nchez[1]; [1]Universidad de ConcepciÛn, Edmundo Larenas 270, Casilla, ConcepciÛn 53-C Chile

Arsenic is one of the main contaminants presents in copper mining resources today and its abatement represents a challenge for metal extraction in the future, particularly under the strong environmental requierements in a global community. The possibility to form ferric arsenate directly from a gas phase by means of a heterogeneous reaction between an arsenic gas bearing and iron oxide was studied at laboratory scale. A thermodynamical analysis for the system Fe-As-O-S has been initially made, in order to obtain the stability conditions for the ferric arsenate or other $Fe_xAs_yO_z$ type compounds. Experiments were made using an hematite sample suspended from a thermogravimetric device, inside a vertical furnace. Gas As4O6 generated from solid As2O3 were passed through the iron oxide sample and its instantaneous weight changes was recorded directly in a computer. A kinetic study for the As4O6 volatilization was made, which shows chemical control between 300 and 600∞C, and with an apparent activation energy of around 14 Kcal/mol As2O3. Samples after reactions were chemically and by XRD analysed. Arsenates detected corresponds to complex compounds. Results shows that formation of compounds depend on temperature and oxygen content of the gas phase. Kinetic for iron arsenates formation is slow, reaching an arsenic capture of 6% after 80 minutes of reaction when an oxygen content of 50% is fed continously at 800∞C. Experiences made at the same temperature but under higher oxygen content in a closed reactor, allowed arsenic capture close to 60%. For higher temperatures capture is notoriously lower.

## Yazawa International Symposium on Metallurgical and Materials Processing: Principles and Technologies: Advances in Non-Ferrous Production Technologies and Industrial Practice: General III

*Sponsored by:* Extraction & Processing Division, EPD-Process Fundamentals Committee, EPD-Pyrometallurgy Committee, EPD-Aqueous Processing Committee, EPD-Copper, Nickel, Cobalt Committee, EPD-Lead and Zinc Committee, Jt. MPMD/EPD-Process Modeling Analysis & Control Committee: See Plenary Session for Co-Sponsors
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Tuesday PM — Room: Point Loma
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*Session Chairs:* Chikabumi Yamauchi, Chubu University, Grad. Sch. of Eng. & Sch. of Eng., Aichi-ken 487-8501 Japan; David G.C. Robertson, University of Missouri-Rolla, Dept. of Metallurgl. Eng., Rolla, MO 65401 USA

**2:30 PM Keynote**
**The Chemistry of Fuming Zinc from Oxide Slags Using Coke**: *David G.C. Robertson*[1]; Dhiren K. Panda[2]; Adrian C. Deneys[3]; [1]University of Missouri-Rolla, Dept. of Metallurgl. Eng., Rolla, MO 65401 USA; [2]Nucor-Yamato Steel, Blytheville, AR 72315 USA; [3]Praxair, Inc., Indianapolis, IN 46222 USA

The key reaction in zinc fuming is ZnO(in slag) + CO = Zn(g) + CO2. This paper includes the results of experiments carried out by the authors. In the first series of experiments it was shown that the reaction 2FeO + ZnO = Fe2O3 + Zn(g) does not occur at an appreciable rate. In the second series it was shown that zinc oxice is not redcued unless a reductant has been added. A third series of experiments was carried out with excess coke. The kinetics of zinc oxide reduction were found to be independent of the zinc oxide concentration, but increased with increasing basicity, and temperature. The presence of high concentrations of FeO in the slag is also known to increase the rate. We propose that, in our work, the kinetics were controlled by a chemical step, namely the rate of desorption of an adsorbed CO2 species.

**3:00 PM**
**Effect of Ultrasonic Wave Irradiation on the Electrical Conductivity of Pure and Sodium Doped Sulfur Melts**: *Nobuaki Sato*[1]; Rajmund Michalski[2]; Takeo Fujino[3]; Yoshio Waseda[1]; [1]Tohoku University, Inst. of Multidisciplinary Rsrch. for Adv. Matls., 2-1-1 Katahira, Aoba-ku, Sendai 980-8577 Japan; [2]Polish Academy of Science, Inst. of Environml. Eng., Skrodowska-Curie 34 St., Zabrze 41-819 Poland; [3]Tohoku University, Inst. for Adv. Matls. Procg., 19-14 Higashioshima, Hitachinaka 312-0042 Japan

Sulfur melt is expected to have a potential use in the materials synthesis field as a molten process, such as a low temperature synthesis of mixed sulfides. If the adiabatic property of the sulfur is improved to have a relatively high conductivity by the irradiation of ultrasonic waves, it would extend to the electrochemical process. In this paper, the electrical conductivity, $\sigma$, of pure and sodium doped sulfur melts was measured in the presence of ultrasonic waves from 433 to 573 K by the two probe method using ultra high resister meter. The $\sigma$ value of the pure sulfur melt with irradiation was jumped at around 443 K by the order of $10^2$ and then monotonically increased from $10^{-5}$ to $10^{-4}$ $Scm^{-1}$ with increasing temperature. The addition of sodium metal to the sulfur melt was proved to be more effective for jumping the $\sigma$ value of the melt to an acceptable level when ultrasonic wave was irradiated.

**3:25 PM Invited**
**Mathematical Modeling of Phase Interaction Taking Place During Fusion Welding Processes**: *Michael Zinigrad*[1]; Vladimir Mazurovsky[1]; Alexander Zinigrad[1]; [1]College of Judea and Samaria, Science Park, Ariel 44837 Israel

The quality of metallic materials depends on their composition and structure and these are determined by various physico-chemical and technological factors. To effectively prepare materials with required composition, structure and properties is necessary to carry out research in two parallel directions: 1. Comprehensive analysis of thermodynamics, kinetics and mechanisms of the processes taking place at the solid-liquid-gaseous phase interface during welding processes; 2. Development of mathematical models of the specific welding technologies. We have developed unique method of mathematical modeling of phase interaction at high temperatures. This method allows us to build models taking into account: thermodynamic characteristics of the processes, influence of the initial composition and temperature on the equilibrium state of the reactions, kinetics of heterogeneous processes, influence of the temperature, composition, hydrodynamic and thermal factors on the velocity of the chemical and diffusion processes. The model can be implemented in optimization of various technological processes in welding, surfacing, casting as well as in manufacturing of steels and non-ferrous alloys, materials refining, alloying with special additives, removing of non-metallic inclusions.

**3:50 PM**
**Green Technology to Recovery Value Metal Compounds from Molten Slags**: *Zhitong Sui*[1]; Li Zhang[1]; Taiping Lou[1]; Zhida Sui[1]; [1]Northeastern University, Sch. of Matls. & Metall., Shenyang 110006 China

Based on several case studies in precipitating behavior of value metal compounds (VMC) in molten slags a green technology to recovery VMC from molten slags is proposed, in which three steps are involved: (1) The selective concentrating of dispersed VMC into the designed mineral phase in molten slag; (2) The selective coarsening of the designed mineral phase to critical grain size in molten slag; (3) The selective separating of the grown mineral phase in solidified slag from tailing by dressing or hydrometallurgy processes. The features of the technology are economic, clean, intensive and comprehensive. The utilization of recovered VMC such as Titanium, Boron, Vanadium, chromium and Iron compounds was summarized as examples of technology application. It was confirmed by experiments that the precipitating of the designed mineral phases like Perovskite (CaTiO3), Suanite (2MgO o B2O3), Spinel (MgO oCr2O3) and Magnetite (Fe3O4) in molten slags are obviously affected by operation factors such temperature, chemical composition, heat-treatment, additives and so on. The precipitating kinetics and mechanism of VMC from molten slags during solidification processes were also investigated.

**4:15 PM Break**

**4:35 PM Keynote**
**Progress and Problems in the Simulation of Non-Ferrous Extraction Processes**: *Arthur E. Morris*[1]; [1]Thermart Software, 12102 Calle de Maria, San Diego, CA 92128-2720 USA

Fifty years ago when Professor Yazawa began his career, the field of process simulation and modeling was in its infancy. Since then, tremendous progress has been made in our ability to model metal production flowsheets from mine to refined metal. This progress has come about by parallel developments in basic understanding of process chemistry and in computational techniques. This paper will review the progress made in process understanding and modeling in lead, zinc, and copper metallurgy from its inception to the present, and the role of Professor Yazawaís work in furthering this progress. Specific examples will be given for the sintering of lead concentrates, slag fuming, zinc concentrate roasting, flash smelting of copper, and pyro-extraction of zinc. Factors limiting further progress will be described.

**5:05 PM**
**The Experiment on Reducing-Matte Smelting of Jamesonite Concentration**: Tang Chaobo[1]; Tang Motang[1]; Yao Weiyi[1]; [1]Central South University, Dept. of Metall., Yuelunanlu, Changsha, Hunan 410083 China

The reducing-matte smelting is a new pollution-free metallurgy technique. In the process pyrite cinder or ferric oxide ore reacts with non-ferrous metal sulphide and produce metal. In this paper, the reducing-matte smelting of jamesonite concentrate has been conducted, and the influences of temperature, amount of pyrite cinder and amount of additive on the smelting process have been studied. Under the optimum technical conditions, the direct recovery ratio of antimony and lead are 83.26% and 68.5%. The ratio of fixed sulfur is 98.97%. It shows that this method is feasible and pollution-free of sulfur dioxide. But the distribution ratio of lead and silver in ferrous matte is 15% and 30%, therefore how to recover lead and silver economically and effectively from ferrous matte is still a problem to be solved.

**5:30 PM**
**Melt AtomisationñThe Bridge from Pyro- to Hydro-Metallurgy**: *J. J. Dunkley*[1]; D. Norval[2]; [1]Atomising Systems, Ltd., Sheffield S9 1EW England; [2]Bateman Pty, Johannesburg S. Africa

Recent years have seen the increased use of hydrometallurgy in the smelting and refining of metals. However this is often used as a final refining step, following an initial pyrometallurgical smelting process. Huge amounts of material are produced as melts which have to be cast, comminuted, and taken up into solution or leached. A common method is to granulate the melt and then grind it. In the case of metallic melts this can be difficult or unfeasible due to the ductility of the granulated particles. Water atomisation is capable of replacing the granulation and grinding stages with a single process step that can process in excess of 30t/hour of melt into particles as fine as 50 microns. Applications in operation in Co, Cu, Ni, Ag, Au, Pt and Rh refining are discussed together with potential applications in copper smelting.

## Notes