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Abstracts
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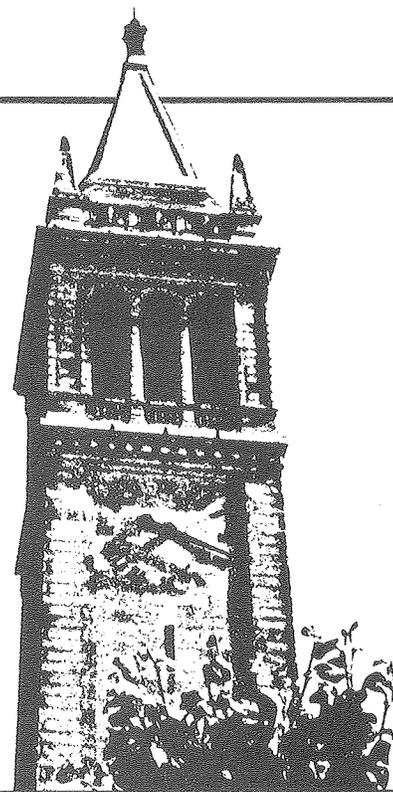
Surfaces and Interfaces in Ceramic and Ceramic-Metal Systems

JULY 28-AUGUST 1, 1980

7th LBL/MMRD International
Materials Symposium

●
17th University
Conference on Ceramics

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Surfaces and Interfaces in Ceramic and Ceramic-Metal Systems

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7th LBL/MMRD International
Materials Symposium

●
17th University
Conference on Ceramics

Department of Materials Science and
Mineral Engineering, College of Engineering

●
Materials and Molecular Research Division
Lawrence Berkeley Laboratory

●
University of California
Berkeley, California

**SURFACES AND INTERFACES
IN CERAMIC AND CERAMIC-METAL SYSTEMS**

July 28 - August 1, 1980

Monday, July 28

8:00 — Registration

Joseph A. Pask, Co-chairman of Symposium

9:00 — Opening of Symposium

9:05 — Welcoming remarks from University of California, A. M. Hopkin, Dean, College of Engineering

9:10 — Welcoming remarks from Lawrence Berkeley Laboratory, Alan W. Searcy, Associate Director and Head, Materials and Molecular Research Division

9:15 — Opening remarks on Symposium

Session Chairman — George C. Kuczynski, Notre Dame University

A. Calculations of Interface/Surface States

9:30 — Pseudopotential Calculations for Ideal Interfaces

Marvin L. Cohen, *University of California at Berkeley.*

10:00 — Energies and Structures of Grain Boundaries, Stacking Faults, and Surfaces in Metal Oxides with NaCl Structure

Dieter Wolf, *Argonne National Laboratory, Argonne, Illinois.*

10:25 — The Nature and Role of Surface Charges in Ceramics

Z. A. Munir, *University of California at Davis,* and J. P. Hirth, *Ohio State University, Columbus, Ohio.*

10:50 — Coffee Break

B. Characterization of Surfaces and Interfaces

11:05 — Physical and Chemical Characterization of Interfaces by Electron Optical Methods

G. Thomas, R. Gronsky, O. Krivanek, and R. K. Mishra, *University of California at Berkeley.*

11:35 — Use of Photoemission and Synchrotron Radiation for Studies of Surfaces and Interfaces

W. E. Spicer, *Stanford University, Stanford, California.*

12:00 — Improved Electrical Characterization of Ceramic Oxides: Bulk vs. Interface Effects

T. Stratton, D. Button, A. McHale, D. Reed, and H. L. Tuller, *Massachusetts Institute of Technology, Cambridge, Massachusetts.*

12:25 — Lunch

Session Chairman — Robert F. Davis, North Carolina State University

C. Thermodynamics of Interfaces

1:45 — Chemical Aspects of Equilibrium Segregation to Ceramic Interfaces

Paul Wynblatt and R. C. McCune, *Ford Motor Company, Dearborn, Michigan.*

2:15 — Interfaces Between Metals and Ceramics

J. T. Klomp and P. J. Vrugt, *Philips Research Laboratories, Eindhoven, NETHERLANDS.*

2:40 — Interfacial Energetics in Metal-Metal, Metal-Ceramic, Metal-Semiconductor, and Related Solid-Solid and Liquid-Solid Systems

L. E. Murr, *New Mexico Institute for Mining and Technology, Socorro, New Mexico.*

3:05 — Coffee Break

D. Influence of Surfaces and Interfaces on Selected Ceramic Processes

3:20 — Adsorption of Dispersants from Non-Aqueous Solutions

E. S. Tormey, L. M. Robinson, W. R. Cannon, A. Bleier, and H. K. Bowen, *Massachusetts Institute of Technology, Cambridge, Massachusetts.*

3:45 — Oxide-Aqueous Media Interfaces and Dissolution Kinetics

D. W. Readey, *Ohio State University, Columbus, Ohio.*

- 4:10 — The Reaction Interface in Reduction
Mei Chang and Lutgard C. DeJonghe, *University of California at Berkeley.*
- 4:35 — Interfacially Controlled Crystallographic Phenomena in the System K_2CO_3 - $KAlO_2$
L. P. Cook, *National Bureau of Standards, Washington, D.C.*
- 5:00 — Development of Surfaces and Interfaces in In-Situ Reacted Mullite-Zirconia Composites
N. Claussen, J. S. Wallace, M. Rühle, and G. Petzow, *Max-Planck-Institut für Metallforschung, Stuttgart, WEST GERMANY.*
- 5:25 — Influence of Chemical Heterogeneity on Sintering
Stane Pejovnik and Drago Kolar, *Institut Jozef Stefan, Ljubljana, YUGOSLAVIA*
- 5:50 — End of day's program
- 6:00 — Wine and Cheese tasting

Tuesday, July 29

Session Chairman — H. Kent Bowen, *Massachusetts Institute of Technology*

E. Grain Boundaries

(a) Structure of Boundaries

- 8:30 — Grain Boundaries in Alumina
A. H. Heuer, *Case Western Reserve University, Cleveland, Ohio.*
- 8:55 — Microstructure and Chemical Composition of Grain Boundaries in Ceramics
M. Rühle and G. Petzow, *Max-Planck-Institut für Metallforschung, Stuttgart, WEST GERMANY.*
- 9:20 — AEM and STEM Investigation of Grain Boundary Segregation in Transition Metal Oxides
Barry Bender, David B. Williams, and Michael Notis, *Lehigh University, Bethlehem, Pennsylvania.*
- 9:45 — TEM Studies on the Structure of Low Angle Grain Boundaries in Nickel Oxide
H. Schmid, N. L. Peterson* and M. Rühle, *Max-Planck-Institut für Metallforschung, Stuttgart, WEST GERMANY, and *Argonne National Laboratory, Argonne, Illinois.*
- 10:10 — Observation on Grain Boundary Structures in Nickel Oxide
K. Y. Liou and N. L. Peterson, *Argonne National Laboratory, Argonne, Illinois.*
- 10:35 — Coffee Break
- 10:50 — Amorphous Grain Boundary Phases in Ferroelectric (PZT) and Ferrimagnetic ((MnZn)Fe₂O₄) Ceramics
R. K. Mishra, E. Goo, and G. Thomas, *University of California at Berkeley.*
- 11:15 — Surface and Interfacial Characterization of Tailored Ceramic Nuclear Waste Forms
Alan B. Harker, David R. Clarke, Carol M. Jantzen, Peter E. D. Morgan, and Ratnakar R. Neurgaonkar, *Rockwell International Science Center, Thousand Oaks, California.*

(b) Boundary Migration

- 11:40 — Diffusion in Migrating Boundaries
J. E. Blendell, W. A. Kaysser and G. Petzow, *Max-Planck-Institut für Metallforschung, Stuttgart, WEST GERMANY.*
- 12:05 — Grain Boundary Migration in LiF
A. M. Glaeser, H. K. Bowen, and R. M. Cannon, *Massachusetts Institute of Technology, Cambridge, Massachusetts.*
- 12:30 — Lunch

Session Chairman — Arthur H. Heuer, *Case Western Reserve University*

(c) Effect on Deformation

- 2:00 — Effect of Grain Boundaries on Creep and Creep Rupture in Ceramics
W. Blumenthal, C. H. Hsueh, J. Porter, A. S. Rana, and A. G. Evans, *MMRD and Department of Materials Science and Mineral Engineering, University of California at Berkeley.*

- 2:25 — Redistribution of Stresses During Creep Bending of Grain Boundary Sliding Materials
J. R. Dryden, Whiteshell Nuclear Research Establishment, Pinawa, Manitoba, and D. F. Watt, *University of Windsor, CANADA*.
- 2:50 — Elastic Creep of Brittle Ceramics with Special Reference to Creep by Crack Growth in Aluminum Oxide
D. P. H. Hasselman, A. Venkateswaran, and C. Shih, *Virginia Polytechnic Institute and State University, Blacksburg, Virginia*.
- 3:15 — Role of Interfacial Defect Creation-Annihilation Processes at Grain Boundaries on the Diffusional Creep of Polycrystalline Alumina
Y. Ikuma and R. S. Gordon, Department of Materials Science and Engineering, *University of Utah, Salt Lake City, Utah*.
- 3:40 — Coffee Break
- 3:55 — The Influence of Grain Boundaries on Creep of KBr
Parviz Yavari and Terence G. Langdon, *University of Southern California, Los Angeles, California*.
- 4:20 — Microstructural Aspects of Creep Deformation in Two-Phases Ceramics
D. R. Clarke, *Rockwell International Science Center, Thousand Oaks, California*.

(d) Grain Boundary Effects on Fracture

- 4:45 — Influence of Grain Boundary Silica Impurity on Alumina Toughness
J. S. Moya, *Instituto de Ceramica y Vidrio, Madrid, SPAIN*, and W. M. Kriven and J. A. Pask, *University of California at Berkeley*.
- 5:10 — Observations and Analysis of the Stability and Nature of Microcracks in Brittle Materials
K. Niihara, J. P. Singh, L. D. Bentsen, and D. P. H. Hasselman, *Virginia Polytechnic Institute and State University, Blacksburg, Virginia*.
- 5:35 — Microcracking in Ceramics
Y. Fu, W. M. Kriven, and A. G. Evans, *University of California at Berkeley*.
- 6:00 — End of day's program
- 7:00 — Banquet at H's Lordships Restaurant, Anthony G. Evans, Co-chairman of Symposium and Toastmaster; Alan W. Searcy, Banquet Speaker.

Wednesday, July 30

Session Chairman — William E. Spicer, Stanford University

F. Si-SiO₂ Symposium

- 9:00 — The Si-SiO₂ Interface: Current Understanding of Chemical and Electronic Defects
Dennis W. Hess, *University of California at Berkeley*.
- 9:30 — Electron Spectroscopy Studies of the Si-SiO₂ Interface
C. R. Helms, *Stanford University, Stanford, California*.
- 9:50 — The Structure of the Si-SiO₂ Interface
O. L. Krivanek, *University of California at Berkeley*.
- 10:15 — Coffee Break
- 10:30 — Chlorine Incorporation and Phase Separation at the SiO₂/Si Interface During Thermal Oxidation of Silicon in Cl/O₂ Atmospheres
M. D. Monkowski, J. Monkowski, R. E. Tressler, and J. Stach, *Pennsylvania State University, University Park, Pennsylvania*.
- 10:55 — Stability Studies of the Chlorine-Containing Phase at the SiO₂/Si Interface Produced by HCl/O₂ Oxidation of Silicon
S. R. Butler, F. J. Feigl, S. A. Titcomb, H. Tsai, *Lehigh University, Bethlehem, Pennsylvania*, and K. H. Jones and H. W. Kraner, *Brookhaven National Laboratory, Upton, Long Island, New York*.

G. Interfacial Phenomena

- 11:20 — Ceramic, Glass and Metal Interfacial Problems in Ceramic Chip Capacitors
M. J. Cozzolino and G. J. Ewell, *Hughes Aircraft Company, Culver City, California*.

- 11:40 — Ceramic-Metal Interfaces in Barium-Bismuth Titanate Multilayer Ceramics
B. S. Rawal, *AVX Ceramics Corp., Myrtle Beach, South Carolina.*
- 12:10 — Interfacial Phenomena in the Chemical Vapor Deposition of Ceramic Thin Films
Robert F. Davis, *North Carolina State University, Raleigh, North Carolina.*
- 12:40 — End of day's program

Thursday, July 31

Session Chairman — Lutgard C. DeJonghe, University of California at Berkeley

H. Formation of Interfaces

- 8:30 — Wetting, Spreading and Reactions at Liquid/Solid Interfaces
J. A. Pask and A. Tomsia, *University of California at Berkeley.*
- 8:55 — Interfacial Phenomena Between a Molten Metal and Sapphire Substrates in P(O₂)
A. C. D. Chaklader, W. W. Gill, and S. P. Mehrotra, *University of British Columbia, Vancouver, CANADA.*
- 9:20 — Wetting of Al₂O₃-Cr₂O₃ Solid Solutions by Molten Copper and Iron
Koryu Aratani, *Research Laboratories of Kawasaki Steel Corp., Chiba, JAPAN,* and Yasukatsu O. Tamai, *Chemical Research Institute of Non-Aqueous Solutions, Tohoku University, Sendai, JAPAN.*
- 9:45 — Influence of Oxygen Partial Pressure on Wettability of Silica by Molten Silver Alloys
A. Passerone, R. Sangiorgi, and R. Minisini, *Centro Studi de Chimica Fisica Applicata, Genova, ITALY.*
- 10:10 — Effect of Oxygen Partial Pressure on Wetting of SiC, AlN and Si₃N₄ by Si and a Method for Calculating the Surface Energies Involved
Michael W. Barsoum and P. Darrell Ownby, *University of Missouri, Rolla, Missouri.*
- 10:35 — Coffee Break

I. Development of Adhesion

- 10:50 — Role of Nickel in the Porcelain Enamelling System
M. A. Salamah and D. White, *Department of Ceramics, University of Leeds, Leeds, ENGLAND.*
- 11:15 — Use of a Flame-Sprayed Undercoat to Improve the Adherence of SiO₂-Al₂O₃ Dental Ceramics on Ni-Cr and Co-Cr Alloys
P. Klimonda, O. Lingstuyt, B. Lavelle and F. Dabosi, *Laboratoire de Metallurgie Physique de l'ENSCT, Toulouse, FRANCE.*
- 11:40 — Alumina Scale Adherence to CoCrAl Alloys and Coatings
D. P. Whittle and D. H. Boone, *University of California at Berkeley.*
- 12:05 — Spreading and Reactions of Molten Metals on and with Cemented Carbides
Kohichi Yajima, Kimio Harano, and Takashi Yamaguchi, *Kaio University, Yokohama, JAPAN.*
- 12:30 — Lunch

Session Chairman — Joseph A. Pask, University of California at Berkeley

J. Reactions at Interfaces

- 2:00 — A Study of Solid State Metal/Ceramic Reactions
R. L. Mehan and M. R. Jackson, *General Electric Company, Schenectady, New York.*
- 2:25 — Solid State Metal-Ceramic Reaction Bonding
F. P. Bailey and W. Borbidge, *CSIRO, Division of Chemical Physics, Clayton, Victoria, AUSTRALIA.*
- 2:55 — High Temperature Metallizing of Alumina
M. E. Twentyman and P. Hancock, *British Ceramic Research Association, Stoke-on-Trent, ENGLAND.*
- 3:25 — Reaction of ZnO on Polished Sapphire Surfaces
Masataka Koumura, Minoru Hashiba, Eiji Miura, Yukio Nirishi, and Taizo Hibino, *Department of Industrial Chemistry, Gifu University, Gifu, JAPAN.*
- 3:50 — Coffee Break

- 4:05 — Electrochemical Oxidation and Dissolution of Single-Crystal UO_2 Surfaces
R. Wang, *Battelle Pacific Northwest Laboratory, Richland, Washington.*
- 4:30 — Interaction of Molten Silicon with Silicon Metal Oxynitride Solid Solutions
R. R. Wills and I. Sekercioglu, *Battelle Columbus Laboratory, Columbus, Ohio.*
- 4:55 — Reactions at Alkali Metal-Glass Interfaces
M. Barsoum, M. Velez, H. L. Tuller, and D. R. Uhlman, *Massachusetts Institute of Technology, Cambridge, Massachusetts.*
- 5:20 — Effect of Thermal History on the Structure of Chemically and Vapor-Deposited Silver Films on Glass
J. E. Shelby, J. Vitko, Jr., and M. C. Nichols, *Sandia Laboratories, Livermore, California.*
- 5:45 — Barium Silicate Glass/Inconel X-750 Interaction
P. V. Kelsey, W. T. Siegel, and D. V. Miley, *EG&G Idaho, Inc., and Idaho National Engineering Laboratory, Idaho Falls, Idaho.*
- 6:10 — End of day's program.

Friday, August 1

Session Chairman — Anthony G. Evans, University of California at Berkeley

K. Mechanical Properties

(a) Fracture Resistance of Interfaces

- 8:30 — Fracture at Interfaces as a Measure of Adherence
S. S. Chiang, D. B. Marshall, and A. G. Evans, *MMRD and Department of Materials Science and Mineral Engineering, University of California at Berkeley.*
- 8:55 — Adhesion of Plasma Sprayed Ceramic Coatings to Metals
C. C. Berndt and R. McPherson, *Department of Materials Engineering, Monash University, Clayton, Victoria, AUSTRALIA.*
- 9:20 — Microstructure and Mechanical Properties of Metal-to-Ceramic and Ceramic-to-Ceramic Joints
G. Elssner, W. Diem, and J. S. Wallace, *Max-Planck-Institut für Metallforschung, Stuttgart, WEST GERMANY.*
- 9:45 — Work of Adhesion Measurements by a Periodic Cracking Technique
Alpertunga Davutoglu and Ilhan A. Aksay, *Department of Metallurgical Engineering, Middle East Technical University, Ankara, TURKEY.*
- 10:10 — Measurement of Thick Film Adhesion by an Impact Separation Technique
William E. Snowden, *Lawrence Livermore Laboratory, University of California, Livermore, California,* and Ilhan A. Aksay, *Middle East Technical University, Ankara, TURKEY.*
- 10:35 — Coffee Break
- 10:50 — Contact Stress and Coefficient of Friction Effects on Ceramic Interfaces
Dave Carruthers, Dave Richardson, and Laura Lindberg, *Garrett Airesearch Manufacturing Company of Arizona, Phoenix, Arizona.*

(b) Surface Effects

- 11:15 — The Influence of Hydrogen on the Surface Integrity of Quartz Crystal Resonators
Jean Flicstein, *Universite de Limoges, Limoges, FRANCE.*
- 11:40 — Environmental Effect on the Mechanical Strength of Glass
Minoru Tomozawa and Yoshio Oka, *Rensselaer Polytechnic Institute, Troy, New York.*
- 12:05 — Effect of Composition and Environment on Lower Limit Crack Growth in Silicate Glasses
C. J. Simmons, S. W. Freiman and Terry A. Michalske, *National Bureau of Standards, Washington, D.C.*
- 12:30 — Lunch

Session Chairman — Hayne Palmour III, North Carolina State University

(c) Oxidation and Interface Effects

- 2:00 — Effects of Oxidation on the Surface and Near-Surface Structure of Silicon Nitride
Nancy J. Tighe, *National Bureau of Standards, Washington, D.C.*
- 2:25 — Effects of Oxidation on the Strength and Fatigue Resistance of Hot Pressed Silicon Nitride
K. Jakus, J. E. Ritter, Jr., and W. Weinraub, *Mechanical Engineering Department, University of Massachusetts, Amherst, Massachusetts.*
- 2:50 — Transient Liquid Phase Bonding of Silicon Nitride Ceramics
R. E. Loehman, *SRI International, Menlo Park, California.*
- 3:15 — Absence of Grain Boundary Film in G. E. SiC
L. U. Ogbuji, *Department of Materials Science and Engineering, University of Florida, Gainesville, Florida.*
- 3:40 — Closing remarks on Symposium
Anthony G. Evans, Co-chairman of Symposium

Pseudopotential Calculations for Ideal Interfaces

Marvin L. Cohen
Materials and Molecular Research Division
and Department of Physics
University of California, Berkeley 94720

ABSTRACT

A review of some of the recent pseudopotential calculations for the electronic structure of ideal interfaces is given. The systems considered are semiconductor-vacuum, semiconductor-metal, and semiconductor-semiconductor interfaces. The calculations yield electronic energy levels, state densities, and charge density plots associated with regions close to the interfaces. The redistribution of charge can be displayed, and those electronic states which localize near the interface (interface states) are easily studied with this scheme. The electronic properties of specific interfaces are studied in detail and used as prototypes to describe the characteristic behavior of a wider class of interfaces.

In general, the discussion is an attempt to describe what state-of-the-art electronic structure calculations can do to explain the observed properties of interfaces in ideal geometric configurations.

Energies and Structures of Grain Boundaries,
Stacking Faults, and Surfaces in Metal Oxides with NaCl Structure*

Dieter Wolf

Materials Science Division
Argonne National Laboratory
Argonne, IL 60439

Abstract

A computer code for the determination of energies and structures of coincidence twist boundaries, stacking faults, and free surfaces in cubic crystals has been developed. An iterative relaxation procedure has been adopted which allows for full relaxation of the ions.

Using the ionic-type potentials of Catlow et al.^{1,2} for NiO and MgO, the energies of (100) and (110) coincidence twist boundaries, stacking faults, and free surfaces have been determined. Our free-surface and stacking fault results are compared with similar calculations by Tasker³ and by Tasker and Bullough⁴ for alkali halide crystals. In contrast to earlier calculations of Wolf and Benedek⁵ on (100) twist boundaries, in the present work ion polarizabilities have been fully incorporated. It is found that due to the large deviation from a cubic environment of the ions in surfaces, the polarizabilities of cations and anions contribute significantly to the relaxed energies of surfaces, stacking faults, and grain boundaries.

For the coincidence twist boundaries considered, the validity of geometrical phenomenological models relating the stability of these boundaries to the density of coincident sites is investigated.

1. C.R.A. Catlow, W.C. Mackrodt, M.Y. Norgett and A. M. Stoneham, Phil. Mag. 35, 177 (1977).
2. C.R.A. Catlow, I. D. Faux, and M. Norgett, J. Phys. C: Solid St. Phys. 9, 419 (1976).
3. F. W. Tasker, Phil. Mag. 39A, 119 (1979).
4. P. W. Tasker and T. Y. Bullough, to be published.
5. D. Wolf and R. Benedek, to be published in Proc. Int. Symp. on "Grain Boundary Phenomena in Electronic Ceramics", Chicago, April 1980.

*Work supported by the U.S. Department of Energy.

THE NATURE AND ROLE OF SURFACE CHARGE IN CERAMICS

Z. A. Munir

Division of Materials Science and Engineering
Department of Mechanical Engineering
University of California
Davis, CA 95616

and

J. P. Hirth

Metallurgical Engineering Department
Ohio State University
Columbus, OH 43210

Abstract

The theoretical developments of the origin and magnitude of surface charges in ceramics will be presented. The role of these charges in evaporation-condensation, grain growth, epitaxy, electrical properties and grain boundary mobility will be reviewed in light of published experimental results on a variety of materials. Recent investigations demonstrating the influence of an external field on the evaporation of (100) surfaces of ionic crystals will be discussed.

Physical and Chemical Characterization of Interfaces
by Electron Optical Methods

G. Thomas, R. Gronsky, O. Krivanek and R.K. Mishra
Materials and Molecular Research Division
University of California
Berkeley, California

ABSTRACT

Great progress has been made in the characterization of ceramics over the past twenty years. Now, with the new generation of high resolution microscopic and spectroscopic electron microscopes we can look forward to an explosion of information parallel to that in metallurgy. In particular, the study of grain boundaries, so critical in ceramic processing and properties, will certainly intensify.

This paper will consider the following factors in relation to such studies.

a) Microscopy:

The limits of physical resolution in electron microscopy (HREM) are now at or near the atomic level. Similar to the work already reported for semiconductors, it should be possible atomistically to characterize grain boundaries at least to $\sim 2.5\text{\AA}$ interpretable resolution. This is particularly important when very small amounts of second phase are present. Several techniques are now available for study, e.g. HREM and dark field imaging using diffuse scattering. Their present limitations and future prospects in HREM will be discussed.

b) Spectroscopy:

Quantities of matter as small as 1000 atoms can be identified by spectroscopic means in an electron microscope. The two principal techniques are energy dispersive X-ray spectroscopy (EDXS) and electron energy loss spectroscopy (EELS). EDXS is more sensitive to elements present in small concentrations (down to 100 ppm), and to heavier elements, while EELS is better for light element identification and the analysis of impurities concentrated into small particles. Examples showing the application of EDXS and EELS to determining the segregation profiles at grain boundaries and the composition of separate grain boundary phases will be presented, with particular emphasis on the distribution of nitrogen in nitrogen ceramics and glasses.

The role of calcium in ceramics is quite intriguing. Three different examples where Ca segregates at boundaries and affects properties will be presented: a) formation of weak calcium silicate phase in refractory Si nitrides, b) segregation of Ca to impair magnetic properties, e.g., in ferrites, and c) precipitation of insulating Cu compounds in β alumina.

This work was supported by the Division of Materials Sciences, Office of Basic Energy Sciences, U.S. Department of Energy under Contract No. W-7405-ENG-48.

USE OF PHOTOEMISSION AND SYNCHROTRON
RADIATION TO STUDY SURFACES AND INTERFACES

W. E. Spicer, Stanford University

By taking advantage of the continuum of radiation (extending into the x-ray region) provided by the intense radiation from an electron storage ring, it is possible to examine rather completely the electronic structure of the last two or three atomic or molecular layers of a solid. By starting with a clean surface and depositing well controlled amounts of a metal or non-metal, the interactions involved in forming specific interfaces can be studied on an "atomic" basis. Examples will be given of the 3-5:metal (e.g. GaAs: Au) and oxide interface where a unified model of Schottky barrier and oxide interface state formation has been developed from such measurements. This model is based on the creation of lattice defects by the ad-atoms. It will be shown that bulk thermodynamics must be used with care and that the surface chemistry and metallurgy cannot be simply deduced from bulk thermodynamical quantities.

IMPROVED ELECTRICAL CHARACTERIZATION OF CERAMIC OXIDES:

BULK vs. INTERFACE EFFECTS

T. Stratton, D. Button, A. McHale, D. Reed, and H. L. Tuller
Department of Materials Science and Engineering
Massachusetts Institute of Technology
Cambridge, MA 02139

The electrical properties of ceramic oxides depend not only on bulk composition but are often sensitive to transport processes occurring at grain boundaries and electrode-sample interfaces as well. In principle, these individual contributions can be separated by performing complex impedance measurements over a wide range of frequencies. In practice, such data are often difficult to interpret due to overlap of electrode, grain boundary and bulk spectra. We report on a 4 probe cross correlator instrument (constructed by us) which overcomes such difficulties by measuring the magnitude and phase of the voltage and current at different electrodes. In this manner, the effects of electrodes on the overall impedance are eliminated.

Measurements of complex impedance have been performed for a number of oxides including stabilized zirconia, tantalum, barium titanate, and fast Li ion conducting borate glasses. The special utility of this instrument in separating electrode from bulk and grain boundary effects will be demonstrated by comparing data obtained both in the 2 and 4 probe configuration as well as results obtained on samples with different geometry or morphology. Data obtained as a function of temperature and oxygen partial pressure are also used to analyze the relative sensitivity of charge transport through the bulk and interfaces on these parameters

CHEMICAL ASPECTS OF EQUILIBRIUM SEGREGATION TO CERAMIC INTERFACES

P. Wynblatt and R. C. McCune

Engineering and Research Staff, Research,
Ford Motor Company, Dearborn, MI 48121

Abstract

Equilibrium segregation to solid interfaces has been the subject of increasing scientific interest over the last few years. This has in large part been the result of a growing experimental capability for the chemical characterization of surfaces and interfaces. Whereas segregation to alloy surfaces and interfaces has been studied widely, there has been relatively little work on segregation to surfaces and interfaces in ceramic and/or other ionic materials.

In this paper, we shall focus on the chemical aspects of equilibrium segregation to grain boundaries and surfaces in ceramics. The paper is divided into two principal sections. In the first of these, we describe the concepts which have been used to interpret interfacial segregation in solids. Brief reviews are included of the classical thermodynamic approach of Gibbs, more recent statistical thermodynamic models based on the regular solution approximation, as well as models developed specifically to deal with electrostatic effects affecting the interfacial composition of ionic solids. The second principal section of the paper reviews some of the salient experimental measurements of equilibrium interface composition in various ceramic and ionic materials. Comparisons between experimental results and the above theoretical framework are provided where possible.

INTERFACES BETWEEN METALS AND CERAMICS

J.T. Klomp and P.J. Vrugt

Philips Research Laboratories, Eindhoven,
The Netherlands

The phenomena occurring when a metal comes in intimate contact with a ceramic at elevated temperatures will be discussed from a thermodynamic point of view. The first step in this process is the disappearance of the free surfaces at the contact area forming an interface by which the system gains energy. The second step in the process is the occurrence of chemical reactions in certain systems. These reactions depend on the atmospheric conditions and can be dissolution- and or redox reactions. Examples for these reactions will be discussed by which use is made of a model of the prediction of the enthalpy of alloy formation ¹⁾. In certain ceramic-metal systems where an oxide melt is used in between the ceramic and the metal one can distinguish between the types of reactions that occur at the metal-melt interface by measuring the EMF of the formation cell metal/oxide melt/inert electrode. Some examples of cells will be given in which oxidation-, dissolution- and redox reactions respectively are observed. The results of the measurements will be discussed.

1) Miedema A.R.; de Boer F.R.; Boom R. Calphad 1 (4),
1977 p341 Pergamon Press.

Interfacial Energetics in Metal-Metal, Metal-Ceramic,
Metal-Semiconductor, and Related Solid-Solid and Liquid-Solid Systems

L.E. Murr

Department of Metallurgical and Materials Engineering
New Mexico Institute of Mining and Technology,
Socorro, New Mexico 87801

Techniques for measuring interfacial energies in metal/metal and metal/ceramic systems utilizing primarily scanning and transmission electron microscopy to examine equilibrium (dihedral) geometries, including groove angles and contact angles are described. Interfacial free energies for contacting systems are described by

$$\gamma_i = (F_{S(1)} - \gamma_{LV(2)} \cos\Omega_c) = (F_{S(1)} - F_{S(2)} \cos\Omega_c)$$

for liquid/solid and solid/solid systems of two components (1,2) respectively. Corresponding adhesive energies are defined by

$$E_{Ad} = \gamma_{LV(M)} (1 + \cos\Omega_c) = F_{S(M)} (1 + \cos\Omega_c)$$

for a liquid or solid metal drop (sessile drop) in equilibrium with a solid substrate respectively. The adhesive energy is measured directly by measuring the contact angle, Ω_c , and substituting the liquid-vapor (LV) surface free energy (γ_{LV}) or the solid-vapor surface free energy (F_S) which can be determined by similar types of equilibrium geometry measurements at a specific temperature. Both the interfacial free energies and the adhesive energies (or work of adhesion) are measured at some equilibrium temperature, and the variations with temperature are also described for certain systems in this work. The temperature coefficients ($d\gamma_i/dT$ and dE_{Ad}/dT) are described for ideal systems, and are reviewed for a number of metal/metal and metal/ceramic systems, specifically Ni/ThO₂, NiCr (80/20)/ThO₂, stainless steel (304)/Al₂O₃. The implications of phase equilibria and miscibility as they influence interfacial energy and energy of adhesion in metal/metal systems are investigated using mercury at room temperature, since γ_{LV} for mercury is known, and F_S for a host of solids (primarily metals) is known. Binary systems studied include Hg/Al, Pd, Mo, W, Pb, Ag, Nb, Ta, C (graphite), Si, NiCr (80/20), 304 stainless steel, and others. Diffusion and alloying are discussed as they influence the interfacial energetics. Examples are also presented of applications in metal/ceramic systems such as dispersion hardened metals and alloys and solar coatings, especially the CrO_x/Cr solar absorber system. A complete review of known values of metal/ceramic and metal/semiconductor interfacial energies and related interfacial phenomena will be presented along with an evaluation of interfacial thermodynamics where possible and appropriate.

ADSORPTION OF DISPERSANTS FROM NON-AQUEOUS SOLUTIONS

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Many ceramic powders are processed using organic solvents. Dispersion of the particles in the liquid depends on the interactions of the powder surface with the solvent and dispersant. The focus of this research is an understanding of the dispersant concentration effects and the powder characteristics (surface impurities, insulator-semiconductor, etc.) on dispersed and flocculated systems.

Charge repulsion and steric stabilization are the two models commonly used to explain the mechanisms involved in dispersion stabilization. Aqueous systems are well described by the double layer electrostatic repulsion model, also known as DLVO theory. In organic media of low dielectric constant, the number of charges per unit volume is lower than in aqueous systems, and ionic stabilization is less likely to be operative. In many non-aqueous systems it is believed that stabilization results from the repulsion between interacting molecules adsorbed onto particle surfaces, steric stabilization. The type of adsorption relevant to this study is that which is usually physical, and occurs from a binary mixture of a surface active agent and an organic solvent onto the powder surfaces. Surface active agents are generally organic materials which are amphipathic in nature. This means that they contain a hydrocarbon group which is non-polar and also a polar group. In relatively non-polar organic solvents, one would expect adsorption of such a surfactant to occur such that the hydrocarbon groups are oriented toward the solvent and the polar groups away from it. Glycerol trioleate and Menhaden fish oil are two substances which have been found to be effective deflocculants.

Menhaden fish oil is a naturally occurring oil which is composed of a mixture of carboxylic ester molecules, including esters of normal monohydric alcohols and triglycerides. The fish oil differs from the glycerol trioleate in that it is composed to triglycerides derived from many different carboxylic acids. The carboxylic acids which make it up are straight chain compounds ranging in chain length from fourteen to twenty-two carbons, including both saturated and unsaturated acids.

Infrared spectroscopy is being used to measure the adsorption of these two deflocculants onto powder surfaces from solutions of an organic solvent. Two different classes of powders were studied: insulating oxide (α - Al_2O_3) and semiconducting oxide (LaFeO_3 - SrZrO_3). The powders and solutions of differing concentrations were mixed for 16 hours at room temperature. After mixing, the dispersions were centrifuged and the supernatant solutions analyzed for concentration using an infrared spectrometer. The peak at 1740 - 1745 cm^{-1} , due to the stretching vibration of the $\text{C}=\text{O}$ group of the ester molecules was used as a measure of the concentration.

The isotherms for the adsorption of fish oil and glycerol trioleate from toluene solutions have very different characteristics (for example, for Al_2O_3 three times less glycerol trioleate is adsorbed at saturation and the concentration dependence of the isotherms are different). The differences in adsorption characteristics are related to the stability of the dispersion and the particle packing geometry of the centrifuged cake. There are also distinctions between the two classes of powder and the treatment of the powder prior to mixing it with the solution.

"Oxide-Aqueous Media Interfaces and Dissolution Kinetics"

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ABSTRACT

The kinetics of oxide dissolution in aqueous systems is of importance in a number of practical situations including metal corrosion, brittle fracture, and the leaching behavior of nuclear waste hosts. A review of the current understanding of the oxide-aqueous solution interfaces and the kinetics of material transport from the solid into solution is presented. In addition recent experimental results on the dissolution kinetics of oxide powders underscore the necessity of careful powder characterization beyond the measurement of surface area.

THE REACTION INTERFACE IN REDUCTION

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ABSTRACT

The kinetics of reduction of dense cobalt ferrite by hydrogen were studied thermogravimetrically in the temperature range from 560°C to 620°C and in the pressure range from 50 to 250 torr. In these conditions, the reduction reaction was found to be under mixed control. The contributions of gas diffusion through the porous metal product layer and of the interface reaction could be separated. It was found that the interface reaction followed Langmuir-Hinshelwood kinetics.

The interface reaction itself could be simply modeled as a combination of a gas/solid reaction and a solid state transport step. Analysis of the pressure dependence of the interface reaction rate parameter indicated that the solid state diffusion step most likely involved cation transport in the metal/oxide interface.

INTERFACIALLY CONTROLLED CRYSTALLOGRAPHIC
PHENOMENA IN THE SYSTEM K_2CO_3 - $KAIO_2$

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ABSTRACT

X-ray data are presented for a series of potassium carbonate/aluminate solid solutions existing at 1100-1300°C within the range 20 - 70 wt% $KAIO_2$ at one atm. The structure of these solid solutions is unusual in that they consist of stacked layers of relatively thick, discrete carbonate and aluminate units. Resulting periodicities (for ordered compositions) have been detected within the range 50 -150A. Optical properties suggest the possibility of potassium ions along the carbonate/aluminate interface aiding in the structural coherence in a manner analogous to that of intercalated compounds. Additional property measurements, structural data and phase equilibrium information are being gathered. The importance of interfacial energetics in determining the stability of this unusual series of substances relative to melt, vapor and other solids will be discussed.

Development of Surfaces and Interfaces
in In-Situ Reacted Mullite-Zirconia Composites

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ABSTRACT

At temperatures above 1430°C zircon and alumina react in the solid state to form a mullite matrix with dispersed zirconia particles. As opposed to the reaction between finely divided alumina and silica powders forming mullite in a powder compact, this reaction occurs rapidly at relatively low temperatures in the pre-sintered bodies. Undoubtedly part of the reason for the rapid reaction is the high density of the bodies before the reaction occurs. As might be expected, particularly at these low reaction temperatures, the reaction products are not the equilibrium reaction products; a wide range of spatially varying alumina:silica ratios exists within the mullite matrix. Also, many of the zirconia particles formed are only partially transformed upon cooling to the stable room temperature crystal structures; in addition to metastably retained tetragonal crystals, there are heavily twinned monoclinic particles as well as particles which contain both monoclinic and tetragonal domains within one coherent particle. Upon further heating at elevated temperatures only minimal growth of the zirconia particles occurs. However, upon cooling there no longer exist the partially transformed monoclinic-tetragonal crystals or the metastably retained tetragonal crystals.

The microstructural development is studied with the art of TEM, including EELS, as well as electron beam microprobe and SEM.

Influence of Chemical Heterogeneity on Sintering

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Grain Boundaries in Alumina

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ABSTRACT

Theoretical and experimental (TEM) studies have been made at the atomic structures of grain boundaries in Al_2O_3 . The theoretical work - the applicability of the coincidence site lattice model - will be discussed and the experimental studies showing dislocation like features in some but by no means all grain boundaries in sintered aluminas will be presented.

Secondly, we have demonstrated that under some conditions MgO can stimulate rather than retard grain growth in polycrystalline alumina, particularly if chemically-induced grain boundary migration can be made to occur.

MICROSTRUCTURE AND CHEMICAL COMPOSITION OF
GRAIN BOUNDARIES IN CERAMICS

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The microstructure of grain boundaries can be studied by means of different techniques of transmission electron microscopy (TEM). The orientation relationship between the two adjacent crystalline grains can be determined by diffraction studies; grain boundary dislocations and other defects associated to the interfaces can be analysed by standardized diffraction contrast experiments. Additional informations on grain boundary structures can be obtained by the direct imaging of the crystal lattice, however, special precautions have to be observed.- The chemical compositions and, especially, the variations of the chemical compositions in ceramics can be determined best by electron energy loss spectroscopy (EELS) studies for light elements. The latter observations were performed at a TEM fitted with a magnetic imaging filter (D. Krahl, K.-H. Herrmann, W. Kunath, Proc. 9th Intern. Congress on Electron Microscopy, Toronto 1978, Vol.I, p.42). The different electron optical methods were applied to NiO, Al₂O₃-ZrO₂ dispersion ceramics, SiC and SIALON ceramics.

In NiO small angle grain boundaries were studied. It could be shown that the planes of the grain boundaries are either the (100) or (110) planes due to intrinsic charging effects. An experiment will be introduced with which charging effects at grain boundaries can be studied.

Different polytypes are observed in SiC prepared with different methods. It can be shown by EELS that in boron doped SiC all additives are concentrated in precipitates (graphite, B₄C) whereas aluminium can be determined in the SiC matrix doped with Al. The grain boundaries of the different materials are studied in details. Amorphous grain boundary layers could not be observed in SiC.

In Si₃N₄ and SIALON ceramics the occurrence of grain boundary layers was studied. It was observed that on small angle grain boundaries and on special grain boundaries (defined similar as in metals) no intercrystalline amorphous phases were observed. On the other hand on all "arbitrary" grain boundaries the intercrystalline films could be analysed. The EELS studies revealed that mainly impurities or sintering additives are concentrated in the intercrystalline phases.

The different observations are compared with other experimental results obtained at the same materials.

ANALYTICAL SCANNING TRANSMISSION ELECTRON MICROSCOPE
INVESTIGATION OF GRAIN BOUNDARY SEGREGATION IN TRANSITION METAL OXIDES

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Recent studies on grain boundary segregation phenomena in Cr and Ti doped NiO will be discussed. A review is presented of specimen and geometry effects encountered in Analytical Scanning Transmission Electron Microscope (ASTEM) studies. This includes problems related to foil thickness and orientation, second phase morphology, x-ray path length, and specimen self-absorption and fluorescence. Calculation methods for the quantitative analysis of intensity data obtained on x-ray absorbing oxide ceramics will be described. Results of experiments quenching samples from different solution temperatures and over a range of cooling rates will be described in relation to available models for grain boundary segregation.

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Abstract:

In deformed and annealed NiO single crystals low angle grain boundaries are observed. Different types of dislocation networks were analyzed in detail by means of HVEM. The Burgers vectors and line directions of the dislocations were determined, including "extraneous dislocations." Twist axes of grain boundaries formed by square networks or hexagonal networks are oriented parallel to $\langle 100 \rangle$ - or $\langle 111 \rangle$ - type directions, respectively. Dislocation reactions are preferentially of the type $\frac{a}{2} (011) + \frac{a}{2} (1\bar{1}0) = \frac{a}{2} (101)$, and under special conditions of the type $\frac{a}{2} (011) + \frac{a}{2} (01\bar{1}) = a(010)$. From tilt experiments we could find out that the grain boundaries are oriented parallel to $\{111\}$ or $\{110\}$ planes, respectively. However, no low angle grain boundary was found on a $\{100\}$ plane. This is in contrast to the expected grain boundary geometry deduced from the observed dislocation networks and can be understood from the strong ionic structure of NiO. The energy of twist boundaries oriented not parallel to a $\{111\}$ plane is enhanced by the formation of "anticoincidence" atomic configurations and it is proposed that this effect is reduced by the introduction of extraneous dislocations into regular networks. For $\{100\}$ faces, however, we assume that due to the strong anisotropy of the surface energy in ionic structures the grain boundary energy is too high to form stable low angle grain boundaries of this type in NiO.

Observation on Grain Boundary Structures in Nickel Oxide*

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ABSTRACT

The relaxation of the long-range strain field near grain boundaries by the formation of structure dislocations has been well established in metals. The structure of the grain boundary dislocation arrays has been shown to be determined by the misfit geometry as well as the interface energy of the grain boundary. Very little data, however, are available for the grain boundary structures in ionic crystals, in which the interatomic interaction is different from that in metals.

Single crystals of nickel oxide were grown by the Verneuil process, and (001) high-angle twist boundaries near coincidence site lattice misorientations have been prepared by a pressure-sintering technique. The structures of the dislocations at the sintered high-angle twist boundaries as well as some subboundaries in the as-grown single crystals were examined by transmission electron microscopy. The strain fields of some grain boundaries were investigated with the boundaries edge-on using a selective area diffraction technique. The observed periodicity of the grain boundary dislocations in nickel oxide and its possible relationship to the magnitude of the elastic distortion near the grain boundaries are described in the paper.

*Work supported by the U. S. Department of Energy.

Amorphous Grain Boundary Phases in Ferroelectric (PZT) and
Ferrimagnetic ((MnZn)Fe₂O₄) Ceramics

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The grain boundary phases in sintered PZT containing
3 wt.% excess PbO and in sintered (MnZn)Fe₂O₄ containing
small amounts of CaO and SiO₂ are characterized morphologically
and microchemically using transmission electron microscopy and
scanning transmission electron microscopy. It is seen that the
additives segregate at the grain boundaries forming a thin amorphous
layer. The role of the additives during sintering, the mechanisms
of the formation of the boundary phases and their effects on the
electrical and magnetic properties will be discussed.

SURFACE AND INTERFACIAL CHARACTERIZATION
OF TAILORED CERAMIC NUCLEAR WASTE FORMS

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Thorough surface and microstructural characterization of a multiphase high alumina tailored ceramic host for simulated nuclear waste and characterization of single phase hosts are being conducted to provide detailed information about the mechanisms for release of waste elements into ground water solutions. The hot pressed, tailored ceramic waste form being studied was developed at the Science Center to physically and chemically immobilize the elements present in existing defense nuclear waste. XRD, XPS, SIMS and STEM analysis techniques are being used to determine the host phases for the waste elements and to assess the roles of microstructural features (grain boundary diffusion, intergranular phases, elemental segregation within individual grains) during the dissolution process. The waste radionuclides Cs and Sr are contained in the ceramic in an unusually flexible magnetoplumbite structure, while U is present in a close packed fluorite structure (uraninite). These phases, among others, are contained within the ceramic matrix of α -Al₂O₃ and (Fe,Mn,Al)-spinel. The tailored ceramic and single host phases are being extensively studied microstructurally before and after exposure to distilled water and reference ground water solutions. The results of these studies are being used to determine the relative contributions of combined physical encapsulation and chemical immobilization in crystalline host phases to retard the release of waste elements and to improve the waste form structure.

DIFFUSION IN MIGRATING BOUNDARIES

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Grain boundary motion during the zincification and dezincification of iron was examined over a range of zinc potentials, all below the solubility limit and below the liquidus. Since at the temperature of the experiments lattice diffusion does not occur, the compositional changes are due to boundary diffusion and boundary motion as was observed by Hillert and Purdy in the same system. This compositionally induced motion was compared in samples with static boundaries prior to the composition change and in samples with already moving boundaries due to recrystallization and grain growth. By examining the concentration profiles behind the moving boundaries, both parallel and perpendicular to the boundary, the diffusivity of zinc in moving boundaries in Fe over a wide range of conditions was determined. This diffusivity is compared to that in static boundaries. Possible atomistic models for grain boundary motion caused by compositional changes will also be discussed.

GRAIN BOUNDARY MIGRATION IN LiF

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ABSTRACT

Grain boundary mobilities were determined for LiF by means of discontinuous recrystallization experiments at temperatures between 350°C (0.55 T_m) and 820°C (0.96 T_m). Measurements were made on single crystals which had been deformed by compressive creep to produce microstructures with equiaxed subgrains. The driving force was varied by changing the subgrain size; a variety of doped and undoped crystals containing from 2 to 300 ppm Mg, or other cation dopants were used.

For most materials the observed mobilities varied by as much as $10^3 - 10^4$ within a temperature range of 200°C or less and do not fit a simple Arrhenius relation. In crystals grown from zone refined starting materials, a systematic effect of reduced mobility with increased Mg doping is observed for a range of temperature and driving force. However, there are substantial effects which are evidently related to background impurities. In comparison, the mobilities observed in "pure" (undoped) UV grade material are much more variable. The results are discussed within the framework of the Cahn impurity drag model; it is necessary to consider solute drag and breakaway from more than one impurity.

The present results are compared with these from other studies on alkali halides. The mobilities in LiF are much lower than measured in KCl using the same technique. The high activation energies and/or relatively low boundary mobilities reported in the literature for KCl and NaCl by-crystals are discussed in light of the present results. Finally, the implication of the results of this study on grain growth and sintering behavior in "real" materials are discussed.

EFFECT OF GRAIN BOUNDARIES ON CREEP AND
CREEP RUPTURE IN CERAMICS

by

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ABSTRACT

High temperature deformation experiments conducted on fine grained polycrystals of alumina have been used to examine cavity evolution at grain boundaries. Cavities with equilibrium and crack-like morphologies have been observed, distributed non-uniformly throughout the material. The role of these cavities in the creep and creep processes are described. A central theme will be the influence of the diffusion inhomogeneity, which is shown to be the source of the cavitation non-uniformity. In particular, transitions from predominantly equilibrium to crack-like cavity morphologies that result from the inhomogeneity are discussed.

REDISTRIBUTION OF STRESSES DURING CREEP BENDING
OF GRAIN BOUNDARY SLIDING MATERIALS

by

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ABSTRACT

A finite element model has been developed to examine the effect of a viscous intercrystalline boundary phase on the distribution of stresses and displacement rates in creep. In particular, the model has been applied to bending creep, where the principal creep mechanism is assumed to be grain boundary sliding. The model predicts that the common practice of calculating the stress distribution using the linear elastic equations is reasonably accurate for the very early stages of creep, but this becomes increasingly inaccurate as strain proceeds. The stress redistribution can be calculated through to failure. Some interesting hysteresis effects found by the authors in the creep bending of Si_3N_4 can be rationalized using the model.

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Elastic Creep of Brittle Ceramics With Special
Reference to Creep by Crack Growth in Aluminum Oxide

by

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ABSTRACT

Brittle ceramics can in general, creep by a number of mechanisms such as dislocation glide and climb and Nabarro-Herring and Coble diffusion. Such materials should however also show creep deformation by a time-dependent change in elastic properties, mainly due to cavity formation, rotation of elastically anisotropic grains and the formation and growth of cracks. Such 'elastic creep' which is recoverable on unloading, should be taken into account in the analysis of creep mechanisms from creep curves.

Creep by crack growth requires relatively little material transport compared to other mechanisms and can be the dominant mechanism at temperatures at which other creep mechanisms are largely suppressed. This hypothesis was verified by compiling creep deformation maps for polycrystalline aluminum oxides based on dislocation mechanisms and various diffusional creep processes such as Nabarro-Herring, Coble, and crack growth by a number of high temperature processes.

Results indicate that, at high stresses, creep by crack growth due to surface diffusion is the dominant mechanism over a wide range of temperatures. This mode of crack growth increases with increasing grain size and is largely suppressed in fine-grained polycrystalline aluminum oxide.

ROLE OF INTERFACIAL DEFECT CREATION-ANNIHILATION PROCESSES AT GRAIN BOUNDARIES ON THE DIFFUSIONAL CREEP OF POLYCRYSTALLINE ALUMINA

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A general analysis of ambipolar diffusional creep theory for a polycrystalline binary ionic compound is presented which takes into account ion lattice diffusion, ion grain boundary diffusion and an interfacial reaction process at grain boundaries for both the anion and cation. Diffusional creep is predicted to be rate limiting under two basic conditions: (1) rapid lattice diffusion in materials with intermediate grain sizes and (2) materials with very small grain sizes provided grain boundary diffusion is very slow. Steady state diffusional creep data will be presented at 1400-1500°C for polycrystalline Al_2O_3 doped with Ti (0.05-0.2 cation %) and a Mg-Ti co-dopant (0.05% Mg-0.05% Ti) which are consistent with interfacial controlled kinetics over an intermediate range of grain sizes (10-100 μm). In the limit of interface controlled kinetics, creep rates vary with the inverse grain size. When lattice or grain boundary diffusion is rate-limiting, creep rates vary with the inverse square or cube of the grain size. A new type of creep deformation map is presented which reveals the range of variables (grain size and impurity concentration) over which interfacial defect creation and/or annihilation processes at grain boundaries are important in the steady state creep of polycrystalline alumina.

THE INFLUENCE OF GRAIN BOUNDARIES ON CREEP OF KBr

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ABSTRACT

Most creep experiments on alkali halides have used single crystal specimens, and only relatively little information is available on the creep characteristics of polycrystalline materials (primarily LiF and NaCl). In addition, there is the possibility of marked differences in impurity content between the single and polycrystalline samples, which makes it difficult to compare the limited data at present available. Accordingly, this paper describes a series of experiments conducted on KBr with the objective of overcoming these difficulties.

Tests were conducted on two different types of specimen. Initially, a series of compressive creep tests was performed on cleaved KBr single crystals with a $\langle 100 \rangle$ loading axis. This orientation leads to slip on the primary $\{110\}\langle \bar{1}\bar{1}0 \rangle$ slip systems, and the steady-state creep rates were measured as a function of stress over the temperature range of 513-933 K. Second, some of the KBr single crystals were machined into cylinders with the $\langle 100 \rangle$ direction parallel to the long axis, and the cylinders were then hot-extruded at 723 K to give a long polycrystalline rod. Following an appropriate annealing treatment, the average grain size of this material was $\sim 550 \mu\text{m}$. Specimens were cut from the rod and creep tested in compression using the same temperature range as for the single crystals.

The experimental results show that, although there are significant differences in the shapes of the creep curves for the two types of specimen, the final steady-state creep rates are very similar. At the lower temperatures, up to $\sim 600 \text{ K}$, the stress exponent is ~ 6.7 and the activation energy is $\sim 105 \text{ kJ mol}^{-1}$. At higher temperatures, the creep exponent is reduced to ~ 4.5 but there is a corresponding increase in the activation energy to $\sim 180 \text{ kJ mol}^{-1}$.

These results are discussed with reference to the creep mechanisms in the two types of specimen. In addition, the role of grain boundary sliding in the polycrystalline material was measured directly by scribing a series of lines on the undeformed specimens parallel to the loading axis. These measurements indicate that sliding makes only a minor contribution to the total strain, although this process tends to increase in importance as the stress level is reduced.

This work was supported by the United States Department of Energy under Contract DE-AS03-76SF00113 PA-DE-AT03-76ER10408.

MICROSTRUCTURAL ASPECTS OF CREEP DEFORMATION
IN TWO PHASE CERAMICS

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Two phase ceramics in which one phase is crystalline and the other non-crystalline constitute an important class of high temperature structural materials, as exemplified by silicon nitride based alloys and certain glass ceramics. The creep behaviour of these materials is complex involving phenomena such as diffusional flow, cavitation and sub-critical crack growth. In order to determine which deformation mechanism dominates during creep the microstructures of an experimental two phase ceramic have been examined by SEM and TEM as a function of temperature. The ceramic, fabricated by sintering together Al_2O_3 powder and powdered barium-strontium glass, was chosen so that the creep experiments could be performed at temperatures at which the deformation properties of the glass phase itself are known. The characteristic microstructures observed will be reported and compared with those previously observed in MgO fluxed silicon nitride alloys deformed in compressional creep at $1400^{\circ}C$.

Influence of Grain Boundary Silica Impurity
on Alumina Toughness

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ABSTRACT

Alumina powders with a particle size ranging from 2 to 5 μm and with SiO_2 as principal impurity (0.15 w/o) have been used. HF 0.2 N-2 h. removed $\sim 95\%$ SiO_2 . Both powders untreated and HF-treated were dispersed in water at high Z-potential values (pH ~ 4.5), in order to avoid agglomerates, dried and hot pressed at 1500°C - 1 hr. The microstructure of both kinds of samples was studied by SEM. The average grain size and density were the following: 3.0 μm , 96.8% th. and 3.7 μm , 94.2% th for untreated and HF-treated samples respectively. The toughness was measured by using the indentation method and the average values obtained were $3.0 \text{ MNm}^{-3/2}$ (untreated), $4.8 \text{ MNm}^{-3/2}$ (HF-treated). SEM analysis showed that the indented crack goes mainly through grain boundary in untreated samples and through grain in HF-treated samples.

TEM/STEM observations on both samples indicated pockets of glassy phase ($< 10^3 \text{ \AA}$) with high silica content frequently occurring at triple points of untreated samples. This glass flux is responsible for the decreasing toughness and fractural behavior of the untreated samples.

Observations and Analysis of the Stability and Nature of
Propagation of Microcracks in Brittle Materials

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ABSTRACT

Inhomogeneous thermal expansions in brittle polycrystalline materials or composites can result in extensive micro-cracking on cooling from the manufacturing temperature.

The formation of micro-cracks in a number of such materials was monitored by measurement of the temperature dependence of the thermal diffusivity by the laser flash method. The experimental results were interpreted in terms of the known theoretical effect of randomly oriented cracks on the thermal conductivity. Depending on the material system, micro-cracks can exhibit a time-dependent growth or healing or a combination of both by diffusional or other processes.

A theoretical basis for these observations was established by analyzing the stability and nature of crack propagation (including sub-critical and unstable) of pre-cursor micro-cracks in a spherical conclusion contained in an infinite with different elastic properties. It is shown that micro-crack formation may require a stage of sub-critical crack growth by diffusional process (or stress corrosion). Crack healing is predicted for micro-cracks which formed in an unstable manner to become subcritical. A statistical size distribution of pre-cursor micro-cracks can lead to simultaneous sub-critical crack growth and healing, in agreement with observations.

It is predicted that due to the existence of sub-critical growth of pre-cursor microcracks, brittle materials with high levels of internal stress may undergo less extensive micro-cracking than materials with lower levels of internal stress. Recommendations are made for the processing of micro-cracked materials with optimum material properties.

MICROCRACKING IN CERAMICS

by

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ABSTRACT

Microcracks have been detected at interfaces in monoclinic ZrO_2 . The microcracks form because of the stresses induced by the formation of variants during the martensitic transformation from the tetragonal phase. This microcrack situation is well defined, and thus, ideally suited for quantitative calculations of microcrack initiation; the results of which have important implications for a wide range of microcrack problems.

Stress calculations have been performed using the Eshelby method and stress intensity factors deduced by a superposition technique. The stress intensity factors that derive from the variant field have been superimposed upon the stress intensity factors pertinent to a pre-existent edge dislocation. The results quantitatively demonstrate that spontaneous microcrack formation at interfacial edge dislocations can occur in this system. The implications of this conclusion for other microcrack problems are discussed.

THE Si-SiO₂ INTERFACE: CURRENT UNDERSTANDING OF CHEMICAL
AND ELECTRONIC DEFECTS

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The silicon-silicon dioxide solid state interface system has been extensively studied over the past twenty years, primarily due to its vital importance in integrated circuit technology. Many of the studies performed have dealt with electrical characterization of this interface, with the result that electronic properties can be accurately and reproducibly controlled by process sequences. These investigations have led to a categorization of electrical charges at the Si-SiO₂ interface, wherein the charges are broadly classified into four major types: mobile ionic charge, fixed oxide charge, interface trapped charge, and oxide trapped charge. These charges differ in their location in the Si-SiO₂ structure, in their ability to diffuse through the SiO₂, in their "net" charge polarity, and in their ability to communicate with the silicon surface.

Most process sequences used to minimize or control electrical charges are empirical, because little detailed chemical knowledge of the electronic defects is available. However, recent quantum mechanical calculations along with varied experimental studies have begun to shed light on possible chemical origins of these charges. These investigations also suggest that some of the charges have common origins in the nonstoichiometric SiO_x region near the Si-SiO₂ interface.

Electron Spectroscopy Studies
of the Si-SiO₂ Interface*

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ABSTRACT

In this paper studies of the Si-SiO₂ interface which have been performed using various electron spectroscopies will be reviewed. An introductory brief discussion of some key experiments which have been performed using other techniques will be followed by a description of the details of electron spectroscopy relevant to the studies of the Si-SiO₂ interface. Results from the numerous studies of the Si-SiO₂ interface that have been performed will then be reviewed with particular attention paid to the chemical nature of the Si-SiO₂ interface and the SiO₂ that exists near the interface.

THE STRUCTURE OF THE Si-SiO₂ INTERFACE

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We have studied several types of Si-SiO₂ interfaces by high resolution electron microscopy (HREM). The interfaces are examined in cross-section at about 3Å resolution, and the structural results are supplemented by other analytical techniques.

High temperature (>1000°C) oxidation of silicon, in both wet and dry atmosphere, was always found to give interfaces with *abrupt* ($\approx 3\text{\AA}$) transition from the crystalline silicon into the amorphous oxide. The *roughness* of the interfaces was $\sim 3\text{\AA}$ r.m.s., with a dominant wavelength of $\sim 50\text{\AA}$, and it was largely independent of the silicon crystal orientation ((1,0,0), (1,1,1), (1,1,0), and (9,1,1) were studied). Lower temperature, ultra-thin ($\sim 30\text{\AA}$) oxide interfaces were also abrupt, but the roughness was slightly greater than 3Å. In addition, a longer wavelength (200-500Å) undulation of $\sim 6\text{\AA}$ amplitude was observed on both types of oxides.

HREM can easily determine the thickness of thin oxides to $\pm 2\text{\AA}$, *independently of the oxide composition*. Correlating the HREM result with a thickness measurement by some other, composition sensitive, technique should therefore reveal the oxide composition and stoichiometry. We have found that ellipsometry measurements are consistent with 30Å oxides being fully stoichiometric, but also that ellipsometry of such ultra-thin films is actually not very sensitive to composition. We are now hoping to determine the oxide stoichiometry by correlating HREM with resonant Rutherford back-scattering.

Chlorine Incorporation and Phase Separation at the SiO₂/Si
Interface During Thermal Oxidation of Silicon in Cl/O₂
Atmospheres

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ABSTRACT

Thermal oxidation of silicon is an important step in the production of semiconductor devices. It has been shown that the introduction of several volume percent of compounds containing chlorine into the oxidizing atmosphere significantly improves the electrical characteristics of these devices. In particular, the chlorine is responsible for the passivation, that is trapping and neutralization, of mobile ionic contaminants that can adversely affect electrical stability.

Earlier investigations using Rutherford backscattering (RBS) measurements have shown that nearly all of the chlorine is contained within 200 Å of the oxide-silicon interface, and scanning transmission electron microscopy (STEM) investigations that we have done have revealed the separation of a chlorine-rich phase into regions approximately 0.5 μm in extent. Most recently, our investigations have used infrared spectroscopy in order to identify the chemical structure of the phase. These observations suggest correlations between phase separation and passivation as well as with other electrical and physical properties, and indicate that it is the development of this chlorine-rich phase near the interface that is responsible for the beneficial effects.

In this paper we discuss these experimental observations and examine possible mechanisms for chlorine incorporation, phase separation, and mobile ion passivation at the oxide-silicon interface.

Stability Studies of the Chlorine Containing Phase at
the SiO₂/Si Interface Produced by HCl/O₂ Oxidation of Silicon

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ABSTRACT

When silicon is oxidized in Cl containing ambients a Cl containing phase has been found to grow at the SiO₂/Si interface (1). Samples consisting of 1500 Å of SiO₂ on (100) Si were prepared by oxidation of Si in HCl/O₂ atmospheres at 1150 and 1200°C. Values of the oxidation parameters were chosen to correspond to those where the Cl containing phase supposedly covers the interface (2). These samples have been annealed in Cl free inert ambients (nominally dry N₂) at similar temperatures to those used in their preparation for times up to 16 hours. The Cl content and distribution have been studied by Rutherford backscattering spectrometry (2.8 MeV α particles) and ellipsometric measurements (3,4). Analysis of the RBS results is carried out by the method of moments. A systematic loss of Cl and changes in the Cl distribution (interpreted as changes in phase morphology) are observed with increasing annealing time. The ellipsometric results show changes in the apparent absorption factor of the SiO₂ film which has been suggested to be due to surface roughness (4).

Computer simulations of the Cl out diffusion from the Cl containing phase have been carried out and compared with the experimental results (5). From these simulations we estimate Cl solubility and diffusivity in the SiO₂. Preliminary agreement at 1200°C gives a solubility of 10¹⁷cm⁻³ and diffusivity of 4 × 10⁻⁹cm²/sec neglecting changes in phase morphology. The results will be discussed in terms of their relationship to the formation and stability of the 3rd phase at two phase SiO₂/Si interface.

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1. J. Monkowski, et al., J. Electrochem. Soc. 125, 1867 (1978).
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"Ceramic, Glass, and Metal Interfacial Problems
in Ceramic Chip Capacitors"

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Multilayer ceramic capacitors are electrically connected to the conducting electrodes using a multilayered glass frit/metal to metal to metal system. As a result of constant industry experimentation to find cheaper systems, inadequate process controls, and an inadequate understanding of the physics of these systems a number of recurring problems are associated with these terminations. Among these problems are: non-wetting of surfaces, degradation of interfacial adhesion with aging, inadequate leach resistance, and stress-cracking of the dielectric under the termination. This presentation will discuss: methods utilized to identify problem causes, test techniques currently used to inspect part lots, and details of the results of these analyses.

CERAMIC-METAL INTERFACES IN BARIUM-BISMUTH TITANATE
MULTILAYER CERAMICS

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Barium-bismuth titanate multilayer ceramics were prepared from 0.6 μm solid state sintered BaTiO_3 with additions of 14% wt. % bismuth titanate and Pd-Ag alloys as internal electrodes. The samples were fired at 1100°C and the ceramic has an average grain size of 1.1 μm .

Both the fracture as well as polished cross-sections and the surfaces cleaved at the ceramic-metal region were examined in the SEM and the micrographs suggest a sharp interface; the corresponding EDS analyses is presented. However, in some cases analyses of ion beam thinned sections in the STEM mode show that there is a series of bismuth containing phases 0.1 to 0.2 μm wide which are formed at this interface. The Bi concentration is unusually high, by as much as a factor of three, in these layers compared to the ceramic matrix. An additional 0.05 μm layer of low z elements was also suspected; no EDS spectra was obtained from these layers. The presence of these unusual phases at the interface were accompanied by variations in the insulation resistance compared to those samples which had a sharp ceramic-metal interface in the STEM mode. Those observations assist in modifying the process so that the performance of the device can be improved. Consistency with the earlier results on grain growth inhibited barium titanate ceramics is established.

Interfacial Phenomena in the Chemical Vapor
Deposition of Ceramic Thin Films

Abstract

A variety of chemical reactions and physical rearrangements occur at the substrate - deposit interface during the hetero- and homoepitaxial chemical vapor deposition of the various ceramic thin films currently being investigated. These processes are primarily a function of the crystallographic orientation, thermal expansion and chemical nature of the substrate surface and the composition of the deposition ambient. They include accommodation, isotropic or anisotropic diffusion, reorganization, nucleation, coalescence, growth and, finally, elastic strain accompanied by the introduction of misfit dislocations. Within the space and time allowed, the author will review the current knowledge of several of the above processes wherein it pertains to particular ceramic thin films and correlate the resulting deposit(s) with that predicted by theoretical CVD phase diagrams currently under development in the author's laboratory. Examples include Si on sapphire and/or spinel, GaAs on spinel and SiC and Si₃N₄ on Si and graphite. A brief discussion or annotated bibliography concerning other chemically vapor deposited ceramics is also contemplated.

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Wetting, Spreading and Reactions at Liquid/Solid Interfaces

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ABSTRACT

Chemical (thermodynamic) stable equilibrium at glass-metal interfaces is established when the liquid glass becomes saturated with the low valence oxide of the metal. Stable or metastable equilibrium conditions at glass-metal interfaces result in a constant contact angle in a sessile drop experiment. If chemical equilibrium is absent, than a driving force exists for the occurrence of a reaction to attain equilibrium. All reactions that take place contribute to the maintenance of the necessary saturation of the liquid and solid at the interface with the solid substrate oxide in order to realize chemical bonding across the interface. Spreading always occurs when the solid metal is an active participant in these reactions. Examples showing the development of these principles are based on systems of sodium disilicate with Fe, Co, Ni, Fe-Ni alloys, Pt, Ag, Au, Cu, Ta, W, Mo, Nb, Zr, and Cr. The final structure and composition of the glass-metal interfacial zone are determined by the kinetics and thermodynamics of the reactions that occur.

Interfacial Phenomena Between a Molten
Metal and Sapphire Substrates in P(O₂)

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ABSTRACT

It has been shown that wettability of a molten metal on a sapphire substrate in P(O₂) can be predicted from the knowledge of some fundamental properties, e.g. γ_{LV}° - the surface tension value of the pure molten metal; γ_{SV} - the surface energy of the substrate and ΔF° 's, free energy of formation of oxides (stable at the temperature) and compounds which are expected to be formed at the solid-liquid interface. The Young-Dupre equation $\gamma_{SL} = \gamma_{SV} - \gamma_{LV} \cos \theta$ has been modified eliminating the experimental parameter ' θ '. The final equation has the form:

$$\gamma_{SL} = \gamma_{SV} - \left[\gamma_{LV}^{\circ} - \frac{RT}{SN} (\ln[O^{2-}] - \ln[O^{2-}]_{crit.}) \right] \cos \left[\frac{(\Delta F_f^{\circ}/T) - b_2}{M_2} \ln[O^{2-}] + b_1 \right] \frac{[O]_{crit}}{[O^{2-}]_{sat.}}$$

where: γ_{LV}° = surface tension in vacuum (erg cm⁻²)

R = gas constant (erg mol⁻¹ K⁻¹)

T = temperature (K)

S = surface coverage (cm²)

N = Avogadro's Number (mol⁻¹)

ΔF_f° = free energy of formation of interfacial compound (kcal mol⁻¹)

b_1, b_2, M_2 = constants

γ_{SV} = surface energy of substrate (erg cm⁻²)

The above equation has been tested for systems with sapphire and Cu, Ni, Fe, Ag, Au and Co. The significance of the constants, b_1, b_2 and M_2 will be discussed.

Wetting of $\text{Al}_2\text{O}_3\text{-Cr}_2\text{O}_3$ Solid Solutions by Molten Copper and Iron

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Effect of Cr_2O_3 content in $\text{Al}_2\text{O}_3\text{-Cr}_2\text{O}_3$ solid solution on wettability by molten copper and iron was investigated by sessile drop method. Some sorts of $\text{Al}_2\text{O}_3\text{-Cr}_2\text{O}_3$ solid solution disks were prepared by coprecipitating hydroxide from the solution of aluminium and chromium nitrate, followed by decomposing, forming and firing. Metal specimen was melted on mirror finished $\text{Al}_2\text{O}_3\text{-Cr}_2\text{O}_3$ solid solution disk at a given temperature in Ar atmosphere, and the image had been photographed at intervals of 5 minutes until equilibrium contact angle was attained. Contact angle and surface tension were estimated from the photographs. Work of adhesion was calculated from the following equation;

$$W_{\text{ad}} = \gamma_1 (1 + \cos\theta)$$

The contact angle of molten copper on the solid solution was independent on Cr_2O_3 content in the solid solution, and the average contact angle was 126° . Whereas the contact angle of molten iron on the solid solution was dependent on Cr_2O_3 content in the solid solution, that is, as the Cr_2O_3 content increases, the contact angle decreases. For instance, the contact angle of molten iron on Al_2O_3 was about 119° , and that on Cr_2O_3 was about 77° .

The work of adhesion of molten copper-solid solution system was independent on the chemical composition of the solid solution, and it was explained in terms of van der Waals energy. On the other hand, the work of adhesion of molten iron-solid solution system was affected by Cr_2O_3 content in the solid solution: the work of adhesion increases as Cr_2O_3 content increases. Cr_2O_3 has a tendency to dissolve into molten iron, and the dissolved oxygen atoms would be adsorbed to surface and interface, and decrease the surface and interface energy. This is the reason why the work of adhesion increases. Thus, in this system, work of adhesion was expressed by the sum of van der Waals energy and chemical interaction energy, and the chemical interaction energy was explained in terms of free energy change by adsorption of dissolved oxygen atoms in molten iron to surface and interface.

Influence of Oxygen Partial Pressure on Wettability of Silica
By Molten Silver Alloys

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ABSTRACT

The wetting behavior of molten silver alloys on vitreous silica has been studied by the sessile drop method.

The aim of this investigation is to clarify the role that additions of elements of different electronegativity and reactivity with respect to SiO_2 have on contact angle and on interfacial tension and adsorption.

Moreover, the status of silica surface has been accounted for, by measurements on "as received" samples and on heat-treated, dehydroxylated specimens.

The results are interpreted in terms of different contributions to interfacial tension of oxides' free energy of formation and of dispersion forces interactions.

The influence of oxygen partial pressure has been studied on pure silver and on binary silver alloys, and contact angles and work of adhesion correlated to oxygen concentration in the molten phase.

Oxygen content of furnace atmosphere has been measured by means of a solid state electrode.

Oxygen enhances the wettability of SiO_2 by molten Ag and its alloys, by means of two mechanisms: it strongly lowers both the solid-liquid interfacial tension by adsorption at the interface, and the liquid surface tension.

All systems have been characterized by optical and electronic scanning microscopy and by EDAX and X-ray diffraction analysis.

The formation of intermediate layers of oxides has been found. In the case of pure silver, silver silicates form; their thickness being a function, at equal times, of oxygen partial pressure.

THE EFFECT OF OXYGEN PARTIAL PRESSURE ON THE
WETTING OF SiC, AlN, and Si₃N₄ BY Si AND A METHOD
FOR CALCULATING THE SURFACE ENERGIES INVOLVED

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ABSTRACT

The surface and interfacial energies of the systems Si-SiC, Si-AlN, and Si₃N₄ have been determined at 1430°C and one atmosphere total pressure by a new method at extremely low oxygen partial pressures. The method involves the measurement of molten silicon contact angles as a function of the oxygen activity of the ambient atmosphere. The contact angles and hence the surface energies were found to be dependent on the P_{O_2} .

The surface energies of SiC, AlN, and Si₃N₄, at 1430°C and a $P_{O_2} = 6 \times 10^{-21}$ were respectively 1844, 2470, and 1150 ergs/cm², and were observed to fall about 70-200 ergs/cm² for every tenfold increase in the oxygen partial pressure depending on the substrate. The quantity of monatomic oxygen adsorbed under these conditions was found to be 0.25, 0.35, and 0.16 of a monolayer for SiC, AlN, and Si₃N₄ respectively. The solid-liquid interfacial energies of the Si-SiC, Si-Si₃N₄, and Si-AlN were found to be about 1215, 664, and 2060 ergs/cm² respectively.

THE ROLE OF NICKEL IN THE PORCELAIN ENAMELLING SYSTEM

by

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Glass coated ferrous metal was being produced commercially by 1840 but it was not until the early years of this century that special additives were used to obtain a bond between the enamel and the metal. The first additive used was cobalt oxide which after some initial disagreement came into general use. This was followed a few years later by nickel oxide which, though believed to be inferior in performance, was cheaper in price. Subsequently these two 'adherence oxides' have usually been used together.

During the development of enamel coated sheet steels attempts had been made to use nickel coated steels but these were unsuccessful and it was not until around 1930 that experiments were carried out with the aim of replacing the adherence oxides by a layer of metal applied to the steel surface. These experiments were successful and with the development of suitable steels led to the production of 'one coat' or 'direct-on' enamels. Once the adherence oxides were no longer required it was possible to have a single coat of enamel which could be white in colour. In this application however only one of the metals was effective - nickel; cobalt has not been shown to promote adhesion when applied as a flash to the sheet steel.

Despite the long history of successful industrial enamelling the basic mechanisms responsible for adherence have always been in doubt. In particular the role of both the adhesion oxides and the nickel flash have been the subject of many investigations. Generally speaking there has been little disagreement over the experimental facts and most of the discussion has centred on the interpretation of the role of cobalt and nickel.

The review will show that although many hypotheses have been suggested to account for the behaviour of these additives in enamelling, none of them is entirely satisfactory. The various hypotheses will be assessed according to the extent to which they account for the following facts:

- (1) that cobalt and nickel oxides are the best adherence oxides,
- (2) that there appears to be an optimum amount of the adherence oxides which should be added,
- (3) that nickel is apparently the only metal which will promote adhesion when added as a flash to the steel surface,
- (4) that many other metals such as gold, copper, silver and aluminium do not require additives to promote adherence.

THE USE OF A FLAME-SPRAYED UNDERCOAT TO IMPROVE
THE ADHERENCE OF $\text{SiO}_2 - \text{Al}_2\text{O}_3$ DENTAL CERAMICS ON
Ni - Cr AND Co - Cr ALLOY.

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In order to improve the adherence of a $\text{SiO}_2 - \text{Al}_2\text{O}_3$ dental ceramic on Ni - Cr and Co - Cr alloys we use a metallic flame sprayed undercoat essentially composed of a Ni - Cr alloy and some ceramics (Al_2O_3 , ZrO_2 , Ni_3Al).

We study the mechanical and physico-chemical properties of this composite, by means of an instrumented four-points bending test, and of the diffusion profiles at the interface undercoat / ceramic using an ionic microscope.

We achieve elevated shear stresses at the interface (50 to 175 MPa) depending on the undercoat composition.

We measure also the elastic modulus of fine ceramic coating (0.17 to 0.43 mm) and we show a lowering of this modulus (13 to $1.5 \cdot 10^5$ MPa) as a function of the increase in depth of the ceramic.

The study of the diffusion profiles at the interface, on various ceramic-metal systems of simpler compositions than the real one, and on the real system itself, points out the leading part played by the chromium diffusion in the adherence mechanism.

ALUMINA SCALE ADHERENCE TO CoCr AL ALLOYS AND COATINGS

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Extended Abstract

Adhesion between surface scale and substrate is an essential requirement of a material possessing good overall oxidation resistance. Poor adhesion can lead to exfoliation of the oxide in response to thermal cycling, or mechanically applied stresses, resulting in enhanced oxidation rates. Marked improvements in scale/substrate adhesion, however, can be achieved via the "active element effect" whereby small (< 1%) additions of an active element such as Y or Hf, or of a dispersed stable oxide such as HfO_2 , Y_2O_3 to a CoCrAl alloy or coating containing sufficient Al to develop a protective Al_2O_3 scale on oxidation, substantially improves the overall oxidation resistance.

The improved scale adhesion largely results from the formation of oxide pegs which grow into the substrate around the internal oxide particles of the active element; void formation at the oxide/substrate interface is also suppressed. The distribution of these pegs is critical and with cast alloys, there are substantial differences between Hf and Y which can be related to the distribution of these elements in the alloy. Y tends to segregate to grain boundaries as an intermetallic yttride, whilst Hf remains in solid solution. Conversion of the metallic Hf addition to an oxide dispersion via a pre-internal oxidation treatment improves the distribution of the oxide pegs and thus the scale adhesion. In PVD coating of similar composition and applied by EB evaporation, the differences in peg distribution are not pronounced. However, a type of peg is also seen to develop in coatings containing either no active element, or elements such as Ti, Si and Zr, which are not, or only marginally, active (their oxides are less stable than alumina). The major difference is that the pegs in these latter coatings are not attached to the surface scale. Peg development in the coatings seems related to the presence of elongated grains of the β - CoAl phase in the coating. With the active element containing coatings this extends right up to the interface with the surface scale. In the others, a zone devoid of CoAl separates the scale from the bulk of the coating.

SPREADING AND REACTION OF MOLTEN METALS ON AND WITH
CEMENTED CARBIDES

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Spreading and reaction of molten metals on and with two-phase materials (basically WC-Co alloys) have been studied with special emphasis on the role of carbide/binder interfaces.

Wetting behavior of molten Cu, Zn, Sn and Ag and their binary alloys on the cemented carbides were studied by sessile drop method with various carbide-binder combinations (WC, TaC, TiC/Co, Fe, Ni). It is shown that the wetting depends on the binder and carbide species as well as on the relative concentration of binder phase in cemented carbides. Generally, TaC and TiC increased the apparent contact angle with more pronounced effect with the latter.

Reaction mechanism of molten metals (Cu and its alloys and Zn) with cemented tungsten carbides are basically grouped into three according to the structure of reaction layers. Addition of TaC and TiC to WC checked the reaction and modified the structure of reaction layers. Results on the effects of binder species, binder content and carbide grain size are in favor of the view that carbide/binder interface plays an important role especially in the reaction with Cu and Cu-base alloys.

Finally, the formation mechanism of lamellar structures observed in the reaction between Zn and cemented tungsten carbides¹⁾ has been proposed based on the above results.

- 1) T. Yamaguchi and M. Okada; Formation of Lamellar Structures in the Reaction Between Cemented Tungsten Carbide and Zinc, J. Amer. Cer. Soc., **61**, 529 (1978).

A STUDY OF SOLID STATE METAL/CERAMIC REACTIONS

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ABSTRACT

A study has been made of the reactions occurring between SiC, Si₃N₄, and reaction-bonded SiC and a model superalloy. The experimental arrangement consisted of bringing small coupons of metal and ceramic together under a pressure of about 7 MN/m², thus simulating a realistic ceramic/metal joint. Temperatures of reaction between 700^o and 1150^oC were studied at times up to 200 hours. To date, most of the experiments and subsequent analysis have involved SiC. SiC and the model superalloy reacted at all temperatures between 700^oC and 1150^oC and seemed to be diffusion controlled. The Si/SiC material reacted more severely, and the Si₃N₄ less severely. Analysis of the reaction products was conducted using microprobe, metallographic, and x-ray techniques.

SOLID STATE METAL-CERAMIC REACTION BONDING

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Abstract

When certain metals and ceramic materials are held in contact and heated, a reaction takes place at the interface. This results in a strong bond being formed which is durable even after long periods at elevated temperatures.

While no macroscopic change can be observed when bonding occurs with the "noble" metals a reaction can be observed directly in the electron microscope at magnifications of several hundred thousand times, where an intermediate liquid phase can be seen to form and run over the surface of the ceramic. This phase does not recrystallize on cooling.

Videotape and cinematographic recording of reactions with various noble metals and ceramics will be shown.

With base metals an apparently different reaction occurs resulting in a macroscopic spinel-type bond being formed. Bonding procedures are common to both reaction types.

Research into, and development work on, reaction bonding of ceramics has covered a wide range of metals and ceramics but platinum, gold, copper and nickel appear to be the most significant industrially.

Observations of interfaces together with details of some specific applications and bond properties will be displayed and discussed.

HIGH TEMPERATURE METALLIZING OF ALUMINA

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In the high temperature metallizing process a thin layer of molybdenum paint is fired onto the surface of a debased alumina (e.g. 95% Al_2O_3) so that the alumina can be brazed to a metal component. During the firing, glass from the alumina migrates into the molybdenum layer and helps it to adhere to the alumina. In previous work it has been shown that it is generally desirable to form a dense glass/metal composite structure in order to get satisfactory adhesion between the metallizing layer and the alumina. The object of this investigation was to see how various seal parameters affect the strength when such a metallizing layer is formed.

Variation of the metallizing conditions showed that both the addition of MnO_2 to the metallizing paint and an increase in the furnace humidity (90% N_2 + 10% H_2), from a dew point of $5^\circ C$ to $20^\circ C$, tended to decrease the amount of Mo-Mo sintering in the metallizing layer and to increase the strengths of ASTM test pieces containing Cu washers. The use of different metal washers in place of Cu also changed the seal strengths but with no single combination of metallizing conditions universally producing the strongest seals. With Cu or Cu - 30% Ni washers fracture generally occurred completely in the alumina while with Mo and Nilo K washers it occurred mainly in the metallizing layer. A simple qualitative interpretation of the internal stresses, which occur in these seals, can be used to explain the fracture position. This leads to the conclusion that the use of different process conditions could weaken or strengthen a seal depending upon the particular combination of seal components.

Reaction of ZnO on Polished Sapphire Surfaces

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ABSTRACT

ZnO powder was heated on sapphire surfaces at 900 to 1300°C for various times. The reaction processes at the contact surfaces of the powdered reactants were observed by SEM as a first step to obtain an understanding of the reaction mechanisms.

The reaction process was divided into three steps on the basis of the morphology of the reaction products. The first step was the heterogeneous deposition of reaction products along the flaws on the polished surface of sapphire and the flattening of the products as they accumulated. Deposits appeared scoriated with small pores at 900 to 1000°C and with large crystalline shapes at 1300°C. All of these deposits had a lower ZnO content than that of zinc aluminate. The second step was the formation of craters by gathering of the small spots deposited on the flattened surface and also oriented growth of rods from the small spots. The oriented rods disappeared with continuation of the process steps, and the assembly of the craters formed a structure like a honeycomb. The cell size in the honeycomb structure was 0.3 to 0.4 μm at the low heating temperature of 900 to 1000°C and grew to 0.6 μm at 1300°C. Addition of LiF to the ZnO powder increased the cell size. The third step was the collapse of the honeycomb structure and the formation of polycrystalline grains. The cell walls of the honeycomb structure seemed to sinter into polycrystalline grains during this step.

Electrochemical Oxidation and Dissolution of
Single-Crystal UO_2 Surfaces

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ABSTRACT

Oxidation and dissolution of UO_2 were investigated by electrochemical techniques with single-crystal UO_2 surfaces. The (111) surfaces of single-crystal UO_2 were anodized, dissolved, and etched between -0.2 and 0.8 V (SCE). Under oxidation conditions, thin films of hydrated uranium oxides were formed, and the initial dissolution was controlled by the oxide film. Surface characterization of the UO_2 surfaces and films by x-ray diffraction, SEM and Auger analyses indicates progressive steps for oxidation and dissolution. Study of the long-term dissolution kinetics was made by monitoring the anodic current density as a function of time. For a period of 2-5 days, large fluctuations of dissolution rate were observed. This can be related to the microstructural instability of the surface films.

INTERACTION OF MOLTEN SILICON WITH SILICON METAL OXYNITRIDE
SOLID SOLUTIONS

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ABSTRACT

The interaction of silicon aluminum and silicon beryllium oxynitride solid solutions with semiconductor grade molten silicon at 1450 C was investigated both under argon atmosphere and under vacuum conditions. The stability of these ceramics is dependent upon their crystal structure and metal cation identity. α' Sialon slowly converted to β' Sialon, as a result of a kinetically controlled reaction mechanism. Molten silicon reacted with β' Sialon materials primarily at the grain boundaries, by preferential dissolution of an amorphous grain boundary phase. Microstructural attack of β' Sibeon was difficult to observe.

Dissolution of aluminum and beryllium from β' Sialon and β' Sibeon is dependent upon atmospheric conditions. For example, the aluminum content of molten silicon increased from 50 to 5000 ppm in changing from an inert gas atmosphere to vacuum conditions. Loss of silicon monoxide from the molten silicon apparently controls the rate of dissolution of aluminum from β' Sialon. The reaction stops once the melt is saturated with oxygen.

REACTIONS AT ALKALI METAL-GLASS INTERFACES

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The discovery of solids which exhibit unusually high ionic conductivities has stimulated efforts to construct high energy density batteries utilizing such solids as the electrolytes. To obtain the necessary high energy densities, highly reactive components such as molten Na or Li metal and molten sulfur are generally used as the reactants. In order to determine whether newly developed fast Li ion conducting glasses can be used in such batteries, we have investigated the reactions that occur at glass-liquid metal and glass-molten salt interfaces.

Because of the potential use of these materials in batteries, the glasses of interest have been tested in molten Li both in the presence of an electric field and under quiescent conditions. Studies were performed over a wide range of current densities, temperatures and times. Resistivities determined under these conditions agreed well with values determined by AC techniques utilizing blocking electrodes. Alkali attack was observed to increase with time and temperature and depended strongly on glass composition. The composition dependence has been explored in a variety of systems including alkali borates, zircoborates and aluminoborates. The kinetics characteristic of the interface reactions have been studied by weight change, measurements, optical microscopy, and scanning electron microscopy. Results will be discussed in terms of diffusion controlled processes which result in coloration and change of phase.

EFFECT OF THERMAL HISTORY ON THE STRUCTURE OF CHEMICALLY
AND VAPOR-DEPOSITED SILVER FILMS ON GLASS

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The effect of thermal history on the properties and structure of silver films on glass has been studied for both chemically and vapor-deposited films. Both types of films exhibit silver agglomeration when heated to temperatures above 200-300°C in air. This behavior is not observed in vacuum or in other gases. The agglomeration observed for vapor-deposited films is fairly uniform over the specimen. The chemically-deposited films exhibit similar agglomeration over a major portion of their area. However, the chemically-deposited films also exhibit small streaks of highly-reflective material, which, under magnification, resemble small comets in that they have a circular "head" and a long, tapering "tail".

The nature of the agglomeration process has been studied in both types of films by a variety of techniques including optical spectroscopy, X-ray diffraction, optical and scanning electron microscopy, Auger analysis, and surface profile measurements. The results indicate that the structure and properties of silver films are strongly dependent upon the technique used to deposit the film.

BARIUM SILICATE GLASS/INCONEL X-750 INTERACTION

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Water reactor safety programs conducted at the Idaho National Engineering Laboratory have required the development of specialized instrumentation not available commercially. The electrical conductivity-sensitive liquid level transducer (LLT) developed for a pressurized water reactor (PWR) environment is an example. The operation of the sensing element or "probe" relies upon the passage of current between the center pin through a ceramic medium to the shell of the probe. When water is present the resulting voltage is low (high conductivity), and visa versa when water is absent. However, a large number of LLTs tested in PWR environments exhibited failures in the ceramic. Therefore, a program to characterize the behavior of the ceramic (a barium silicate based glass with minor amounts of TiO_2 , CeO_2 , As_2O_3 , Bi_2O_3 , and Al_2O_3) to metal (Inconel X-750) interface was initiated in order to provide data for optimizing the fabrication parameters of the probe.

Sessile drop experiments at 1273, 1323, and 1373 K at oxygen partial pressures of 0.5, 10^{-3} , 10^{-6} , 10^{-12} , 10^{-15} , and 10^{-19} atmospheres show a decrease in wetting as the oxygen partial pressure is lowered (in both static and dynamic atmospheric changes). The change in contact angle is a result of an oxygen partial pressure below the equilibrium oxygen partial pressure for dissociation of As_2O_3 , and Bi_2O_3 to oxygen and the elemental metal. Elemental analysis via energy dispersive x-ray analysis of sessile drop specimens indicates a deposition of arsenic and bismuth upon the glass surface at oxygen partial pressures less than 10^{-6} atmospheres. The metallic coating on the glass inhibits solution of the prepared metallic oxide of the substrate (Inconel X-750) into the glass.

While optimum wetting is obtained by firing in air (or relatively high oxygen partial pressures), the best bond between the glass and metal, as determined by thermal shock and tensile data, is obtained by pre-oxidizing the metal at oxygen partial pressures less than 10^{-15} atmospheres, and then firing the LLT assembly in air ($\sim 1350K$).

FRACTURE AT INTERFACES AS A MEASURE OF ADHERENCE

by

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ABSTRACT

An indentation method has been used to measure the fracture resistance of interfaces. The method exploits the stable growth of lateral cracks (especially along low toughness interfaces) following the creation of a plastic zone by indentation. The characterization of the procedure is based upon a stress analysis of elastic/plastic indentation and upon the mechanics of crack extension. The stress analysis provides the rationale for the location and initiation of the interfacial lateral cracks. A determination of stress intensity factors then provides a basis for quantifying relationships between the lateral crack length and depth and the interface toughness. The trends in cracking behavior are described and compared with the experimental observations.

THE ADHESION OF PLASMA SPRAYED CERAMIC COATINGS TO METALS

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Plasma sprayed coatings are widely used to provide surface protection but the factors controlling one of their most important properties from the practical point of view, adhesion to the substrate, are not well understood. A pre-requisite for the study of the mechanism of adhesion is a reliable method for the measurement of a parameter related to the removal of a coating from its substrate under controlled conditions. For a variety of reasons the tensile tests commonly employed for measuring coating adhesion do not provide suitable data and a fracture mechanics approach has therefore been examined. A double cantilever beam configuration has been employed to determine the critical strain energy release rate (G_{IC}) for both adhesive and cohesive fracture modes of plasma sprayed alumina, steel and nickel-aluminium coatings on grit-blasted steel. It has been found that adhesive failure occurs at significantly lower values of G_{IC} than cohesive failure, and that G_{IC} is lower for alumina than metallic coatings. These results are in agreement with service experience and suggest that G_{IC} is a useful parameter related to coating adhesion.

The fracture surfaces have also been examined by scanning electron microscopy and related to G_{IC} . Plasma sprayed coatings have a lamellar microstructure formed by the impact and rapid solidification of individual liquid droplets. Cohesive failures occurred predominantly between lamellae for all materials examined, the major differences between alumina and metallic coatings being some fracture of lamellae in the former case and evidence of their plastic deformation in the latter. These observations are consistent with the considerably higher G_{IC} values for metallic coatings. Adhesive failures occurred partly along the substrate interface and partly between coating lamellae and again the higher values for G_{IC} for the metallic coatings could be explained by lamellar deformation. In the case of alumina coatings on nickel-aluminium "bond-coat" the fracture path for adhesive failure of the alumina passed between lamellae in both materials which is consistent with the higher G_{IC} value compared with alumina sprayed directly onto a steel substrate. These results provide an explanation for the superior adhesion of composite metal-ceramic coatings to metallic substrates.

MICROSTRUCTURE AND MECHANICAL PROPERTIES
OF METAL-TO-CERAMIC AND CERAMIC-TO-CERAMIC JOINTS

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Materials joints with a ceramic component are manufactured by high vacuum solid-state bonding. Sandwichlike specimens from bulk HP-Si₃N₄, RB-Si₃N₄, and hot-pressed α -SiC with an intermediate refractory metal layer (Zr, Nb, Ta, Mo) are investigated. The microstructure of these different types of metal-to-ceramic joints is determined by the conditions of the welding process. The bonding behaviour is influenced both by the physical and chemical properties of the components. A pronounced interaction between the bonding behaviour and the impurity content of the ceramic material was observed. The bond strength of the joint was investigated. A method is given for the experimental determination of the correction functions for composite bend test specimens. Young's modulus and compliance were measured with a high precision testing tool. The evaluation of these experiments was performed by computer aided on line data acquisition. Ceramic-to-ceramic joints were made from Refel SiC bonded to itself and the fracture resistance of the bond was measured as a function of the thickness of an intermediate thin Si layer. In addition sandwichlike specimens are made from dense polycrystalline alumina with a bimodal grain size distribution (99.7 % Al₂O₃) and from high-purity fine-grained hot-pressed alumina. The microstructure of the interface region is demonstrated by optical and scanning micrographs. Fracture resistance data of these Al₂O₃ joints are also given.

The Work of Adhesion Measurements
by a Periodic Cracking Technique

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ABSTRACT

A periodic cracking technique which was successfully used in determining work of adhesion of thin brittle films on low-modulus polymeric substrates¹ has been applied to ceramic film-metallic substrate case. The original model assumes elastic behavior of the composite and is insufficient for such an application since the substrates exhibit plastic deformation before adhesive failure takes place. However, the model is quite sufficient for obtaining relative magnitudes of the work of adhesion values. A knowledge of the material properties and the critical stretching force required to peel off the film is sufficient for the calculation of the work of adhesion. A periodic cracking of the film takes place before peeling off. The technique has been used to study the adhesion characteristics of the aluminum/glassy selenium system. The work of adhesion value for the Al/Se interface, where Se was vacuum deposited on electropolished Al, was found to be 100 ergs/cm². On the other hand, when the same substrates were first coated with a fresh layer of Al before Se deposition, a two-fold increase in the work of adhesion was measured by this periodic cracking technique while measurements by a thermodynamic technique (contact angle) indicated a ten-fold increase. The formation of an aluminum selenide compound determined by X-ray photoelectron studies was shown to be the cause of the ten-fold increase measured by the contact angle technique. In the mechanically tested specimens, however, the failure took place (as shown by SEM studies) at the oxidized Al/fresh Al interface since this interface was the weakest component of the laminated system.

1. Chow, T.S., Liu, C.A., and Penwell, R.C. "Direct determination of interfacial energy between brittle and polymeric films," J. Polymer. Sci. 14,1305-1310 (1976).

Measurements of Thick Film Adhesion
by an Impact Separation Technique

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ABSTRACT

Adhesion of glassy Se films to borosilicate glass and LEXAN polycarbonate substrates was evaluated using an impact separation technique. Experimental results were analyzed using a finite-difference computer program, and values for force of adhesion were obtained for various film thicknesses. Selected interfaces were examined using ESCA, and wetting experiments were also performed.

Contact Stress and Coefficient of
Friction Effects on Ceramic Interfaces

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ABSTRACT

High temperature structural application of ceramics involves ceramic-ceramic and metal-ceramic interfaces. In applications such as heat engines chipping and cracking often occur at these interfaces where aerodynamic loads and differential thermal movement produce simultaneous normal and tangential forces. A hypothesis of the chipping mechanism will be presented as will experimental results from a test apparatus designed to evaluate interface compatibility. Results include the influence of contact geometry, temperature, load, dwell time at temperature, number of cycles, lubricants and interface layers on the static and dynamic coefficient of friction and the material strength.

The Influence of Hydrogen on The Surface
Integrity of Quartz Crystal Resonators

by

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Sawn faces and edges of AT-cut quartz crystal blanks have been examined for microcracks. Results of Scanning Electron Microscopy (SEM) after each of the polishing stages, etching or beveling, show oriented microcracks. It is suggested that this is a consequence of Rebinder-Westwood environmental effect which is probably produced by hydrogen diffusion in the near interface region from liquid environments in the zero zeta potential. The initial condition was interpreted as exposure to a hydrogen bearing liquid when the directional intrinsic properties of the quartz single crystals are different in the edges and for the different strain rates as compared to the other crystallographic directions. Cracks propagate more rapidly during the etching stage via the same embrittling effect of hydrogen in a different liquid environment (ammonium bifluoride solution) and so we have found edges to be broken. Further, during the service time of the quartz crystal resonator, may result losses of the material. The losses of quartz in time may explain the source of the aging phenomenon, in quartz resonators.

ENVIRONMENTAL EFFECT ON THE
MECHANICAL STRENGTH OF GLASS

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Mechanical strength of glass is strongly influenced by the environment in which it is measured. For example, the strength in water is far less than that in vacuum. This is usually explained in terms of the stress corrosion mechanism by Hillig and Charles. But the strength reduction is also observed in organic liquid which does not react with glass. An alternative explanation was offered by Orowan who believes that the surface energy term in the Griffith equation becomes smaller in water. The surface energy in the Griffith equation, however, is the fracture surface energy and should be material's characteristic independent of environment. Thus at present no satisfactory explanation exists for the environmental effect on the mechanical strength of glass.

Earlier, the authors found that the mechanical strength variation in liquids is closely related to the swelling or the expansion of porous glass immersed in various liquids. The swelling was caused by the reduction of the surface energy at glass-liquid interface.

Several mechanisms by which the surface energy influences the mechanical strength of brittle material were proposed. They are i) modification of local stress at a crack tip, ii) modification of elastic energy near a crack and iii) modification of the radius of curvature at a crack tip. All these mechanisms predict the reduction of mechanical strength by the reduction of the surface energy, consistent with the experimental observation.

Effects of Composition and Environment on Lower Limit
Crack Growth in Silicate Glasses

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ABSTRACT

Crack growth data was taken for a number of glass compositions using a double cantilever beam technique on specimens immersed in various solutions, e.g. 1.0 Molar Cs^+ or 1.0 Molar Li^+ ions in different pH. Crack velocities were determined in the range 10^{-10} to 10^{-3} m/sec., with particular emphasis on the 10^{-10} to 10^{-8} m/sec. range. It will be shown that the behavior of a glass in this low crack growth regime is highly dependent on its corrosion characteristics. Ion exchange processes will be demonstrated to control crack velocities at higher growth rates, while the rate of silica dissolution controls in the lower range.

In particular, it will be shown that soda borosilicate glasses show a definite crack arrest at stress intensities below a threshold value for all of the solutions investigated. On the other hand, soda-silica and lithia silica binary glasses exhibit a plateau in crack velocity in the 10^{-10} to 10^{-8} m/sec. range, which depends strongly on the pH of the solution. Transitions between crack rounding and crack sharpening will be shown to explain the experimental crack growth data. Fractographic analysis of the DCB specimens will be used to confirm the occurrence of crack arrest in particular glasses.

Effects of Oxidation on the Surface and Near
Surface Structure of Silicon Nitride

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Abstract

Oxidation in air at temperatures up to 1400°C can affect the strength of reaction bonded, and magnesia and yttria-doped hot-pressed silicon nitride by changing the surface and near surface microstructure. A silica scale such as that formed on reaction bonded silicon nitride can blunt the surface cracks which result from machining and thus cause strengthening. The more complex oxide scales which form on hot-pressed silicon nitride can have either a weakening or strengthening effect depending on the time and temperature of the exposure; and on the impurity content and distribution in the material. Serial sections of samples oxidized up to 1000 hours were examined by transmission electron microscopy (TEM and STEM) in order to identify the phases and to study the oxide-oxide and oxide-silicon nitride interfacial interactions. The microscopy results are correlated with observed strength changes.

The Effects of Oxidation on the Strength and
Fatigue Resistance of Hot Pressed Silicon Nitride

by

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The fatigue strength of as-machined and preoxidized hot pressed silicon nitride* (HPSN) was measured in three point bending at temperatures of 23, 800, 1000 and 1100°C as a function of stressing rate. Preoxidation at 980°C for 50h significantly increased the fracture strength for the test temperatures of 23 and 800°C; however, at 1000 and 1100°C the strengths of preoxidized and as-machined HPSN were statistically identical and significantly less than the room temperature strength. The fatigue resistance of the preoxidized specimens was found to be the same as that of the as-machined specimens at all temperatures with both exhibiting a high fatigue resistance ($N \approx 100$) at 23 and 800°C and a significant decrease in fatigue resistance ($N \approx 20$) at 1000 and 1100°C. Thus, it appears that there is no advantage in preoxidizing HPSN to improve its high temperature strength and fatigue resistance.

Predicted fatigue strength distributions using fracture mechanics theory agreed well with the experimental data for as-machined HPSN at all temperatures and for the preoxidized HPSN at room temperature. This implies that at these conditions failure occurs due to subcritical growth of preexisting flaws. The strength distributions of the preoxidized material at 1000 and 1100°C were identical to the distribution at room temperature, suggesting that preexisting flaws are not strength determining at these temperatures. Instead, it is believed that flaw generation by oxidation and subcritical crack growth of preexisting flaws are competing processes at elevated temperatures and fracture strength is determined by the more dominant of these processes. For example, the strength of preoxidized HPSN at 800°C was governed by preexisting flaws at a relatively fast stressing rate; whereas, at a slow stressing rate fracture was dominated by oxidation flaws.

Proof testing at room temperature was effective in eliminating weak samples from the as-machined population at 23 and 1000°C and from the preoxidized population at 23°C. Proof testing did not improve the strength at 1100°C of the as-machined and at 1000 and 1100°C of the preoxidized populations. These proof testing results are in agreement with the above observation on the relative effects of flaw generation by oxidation and subcritical crack growth on the high temperature strength of HPSN.

*Norton NC-132

Transient Liquid Phase Bonding of Silicon Nitride Ceramics

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ABSTRACT

Transient Liquid-Phase Bonding describes a process using oxynitride glass compositions which melt and wet Si_3N_4 when heated and then, on further reaction, either disappear into the bulk or form other desired refractory phases. Such reactions occur between Si_3N_4 powder particles and intergranular liquids during densification and are the basis for all silicon nitride hot pressing and sintering. Since the bonding composition is very similar to that already present intergranularly in Si_3N_4 , it is possible in principle to homogenize the join so that the original boundary disappears. Alternatively, the sealing composition can be adjusted to crystallize specific refractory oxynitride compounds in the boundary.

Reaction-bonded, hot-pressed and sintered silicon nitride have been joined using the Transient-Liquid Phase Bonding technique. Butt-sealed specimens tested by four point bending show breaking strengths greater than those reported in the literature for other joining methods. Furthermore, fracture occurred in the Si_3N_4 and not in the boundary in our tests. Microscopic examination of the interface region shows the boundary is diffuse, in accord with the explanation advanced above. We are continuing our studies of these reactions in order to gain a better understanding of the bonding mechanism.

ABSENCE OF GRAIN BOUNDARY FILM IN G.E. SiC

by

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Abstract

High-angle grain boundaries in G.E. (Sintered and Hot-pressed) SiC were investigated by light-optical and transmission electron microscopy for possible glassy films indicative of liquid-phase densification, which has been proposed to account for the beneficial roles of boron and carbon. The high-resolution TEM techniques employed are capable of revealing the thinnest grain boundary phases. None was found in the G.E. materials, and the suggestion of liquid phase sintering must be rejected.

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