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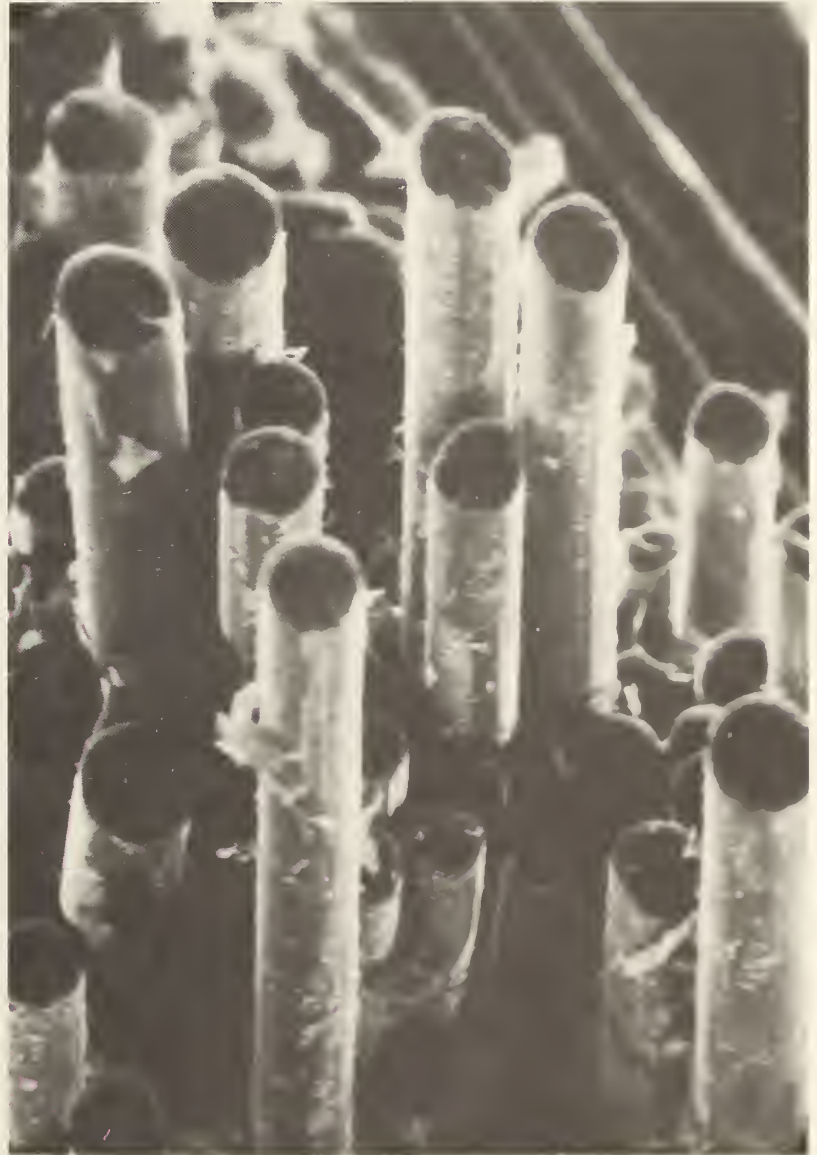
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Reference

Institute for Materials Science and Engineering

NBS
PUBLICATIONS

CERAMICS



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National Bureau of Standards

Technical Activities
1985

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Institute for Materials Science and Engineering

CERAMICS

S. M. Hsu, Chief
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NBS
RESEARCH INFORMATION
CENTER

February 1986

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U.S. Department of Commerce
National Bureau of Standards

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INTRODUCTION

The Ceramics Division has been restructured with two factors in mind:

- o Interest in ceramics continues to grow within the scientific community; in diverse, highly technical segments of American industry; and in the Federal agencies. This growing interest requires close internal coordination of the Division's programs to assure that they continue to be responsive to rapidly evolving national interests and needs.
- o The probability that a Department of Commerce budget increase for advanced ceramics would be funded in fiscal year 1986 has grown throughout the year. Careful program growth will require a broader leadership involved in the response to the increasing national interest.

In order to address these factors, ten groups have been established under the leadership of highly respected scientists. The programs of these ten groups encompass areas of primary importance in electronic and optical as well as structural materials.

The overall objective of the Division's activity is to provide scientific understanding, detailed measurement methods, standard reference materials and standard reference data to enable U.S. industry to achieve key properties of inorganic materials through advanced processing.

Four groups provide services primarily in the property and performance area. In addition to well established groups in Mechanical Properties and in Tribology, the Glass and Composites Group is focusing attention on the role of interfaces in atmospheric effects of fracture, with particular emphasis on composite materials. A new group has been formed to provide for the Division's well-established program in optical materials.

Four additional groups furnish services primarily in the structure and stability area. In the High Temperature Chemistry group, the joint American Ceramic Society/NBS phase diagram program is placing emphasis on non-oxide materials and on materials of electronic and optical importance. The Structural Chemistry group is concentrating its high pressure expertise on stabilization of high pressure phases for advanced processing of tough ceramics. A new group on Ceramic Powder Characterization is providing strengthened interaction with the Joint Committee on Powder Diffraction Data Center. The Surface Chemistry and Bioprocesses group is developing new capability for surface characterization applicable to advanced ceramic powders.

In the processing area, two new groups have been organized to study fundamental sintering processes and to bring advanced concepts of molecular-level chemistry to bear on ceramics. These groups are working closely with their colleagues in American industry, the university community, and other Federal agencies to assure that measurement services to support the development of new ceramics are available in a timely manner. Close

interaction with the National Research Council Board of Assessment in Materials Science and Engineering is one important way in which this assurance can be provided.

In addition to publications, technical society leadership, and scientific collaboration, identified at the end of this report, the Division collaborates with professional colleagues in other traditional ways. Division staff gave more than sixty invited talks to industrial laboratories, independent research institutions, universities, and professional societies, in the U.S. and abroad. The Division organized three major conferences, one on Basic Properties of Optical Materials, one on Biologically Induced Corrosion and one on Ceramic Tribology.

Stephen M. Hsu
Chief
Ceramics Division

September 5, 1985
Updated, January 20, 1986

RESEARCH STAFF

PROPERTIES/PERFORMANCE

Mechanical Properties

- | | |
|------------------------|---|
| Chuang, Tze-Jer | <ul style="list-style-type: none">● Ceramics● Diffusional crack growth● Finite element analysis● Creep theory |
| Chuck, Leon | <ul style="list-style-type: none">● High temperature mechanics● Scanning electron microscopy● Acoustic monitoring of cracks |
| Fairbanks, C. J. | <ul style="list-style-type: none">● Microstructure/strength relations |
| Hockey, Bernard | <ul style="list-style-type: none">● Ceramics● Deformation and wear● Scanning and transmission electron microscopy |
| Krause, Ralph F. | <ul style="list-style-type: none">● Chemical equilibria● High pressure-high temperature testing● Vapor pressure measurements● Refractories |
| Lawn, Brian R. | <ul style="list-style-type: none">● Microstructure/strength relations● Fracture mechanics● Contact phenomena● Surface forces in fracture |
| McDaniel, Clyde | <ul style="list-style-type: none">● Ceramics● Creep● X-ray diffraction |
| Roach, David | <ul style="list-style-type: none">● Surface forces in fracture● Fracture mechanics |
| Tighe, Nancy J. | <ul style="list-style-type: none">● Ceramics● Creep at high temperatures● Mechanical properties, high temperature● Scanning and transmission electron microscopy |
| Wiederhorn, Sheldon M. | <ul style="list-style-type: none">● Ceramics● Erosion● Fracture processes● Mechanical properties at high temperature and pressures |

Glass and Composites

- | | |
|-----------------------|---|
| Blackburn, Douglas H. | <ul style="list-style-type: none">● Special glass formulations● Glass processing● Glass standards for microprobe analysis |
|-----------------------|---|

- Cellarosi, Mario J.
- Glass SRM development
 - Glass standards for manufacture and use
 - Glass property measurements
- Freiman, Stephen W.
- Ceramics and glasses
 - Fracture mechanics
 - Mechanical properties, environmental effects
- Inglehart, Loretta L.
- Thermal wave analysis
 - Nondestructive evaluation
 - Ceramic materials
- Swanson, Peter L.
- Ceramic fracture
 - Microstructure
 - Geologic materials
- White, Grady S.
- Ceramics and glass
 - Nondestructive evaluation
 - Subcritical crack growth

Tribology

- Gates, Richard
- Friction and wear of materials
 - Wear mechanisms and analysis
 - Engine condition monitoring
 - Ferrography
- Hsu, Stephen M.
- Tribology
 - Oxidation mechanisms of organic mixtures
 - Lubrication and wear mechanisms
 - Molecular structural effects on friction
 - High temperature ceramic wear
- Jewett, Kenneth L.
- Organometallic speciation
 - Oxidation kinetics
 - Analysis of organic mixtures
 - SRM research
- Ku, Chia-Soon
- Oxidation kinetics
 - Friction and wear test development
 - Modeling of reaction systems
- Munro, Ronald G.
- Theory and modeling
 - Tribology
 - Molecular dynamics of phase stability
 - Temperature modeling of ceramic pairs
- Pei, Patrick
- Separation of complex organic mixtures
 - Trace organic compound identification
 - Differential scanning calorimetry

Optical Properties

- Farabaugh, Edward N.
- Thin film deposition and analysis
 - X-ray diffraction analysis
 - Scanning electron microscopy
 - Surface analysis
- Feldman, Albert
- Optical materials
 - Thin films
 - Solid state physics
 - Photoelasticity and thermo-optics
 - Guided waves
- Frederikse, Hans P. R.
- Electrical and mass transport in solids
 - Electrical conductivity
 - Depth profiling (Rutherford backscattering)
- Steiner, Bruce W.
- Calorimetric absorption
 - X-ray topography
 - Optical materials

STRUCTURE/STABILITY

High Temperature Chemistry

- Bonnell, David W.
- High temperature-pressure mass spectrometry
 - Computer modeling
 - Levitation calorimetry
- Cook, Lawrence P.
- Phase equilibria of ceramics (modeling and experiment)
 - Phase diagrams for ceramists data center
 - Electron microscopy
 - Thermodynamics
- Hastie, John W.
- High temperature chemistry of ceramics
 - Ceramic phase equilibria and solution models
 - High temperature-pressure mass spectrometry
 - Chemistry of combustion
- Ondik, Helen M.
- Phase diagrams for ceramists data center
 - Materials properties for coal conversion
 - Data compilation systems
- Plante, Ernest R.
- High temperature chemistry of ceramics
 - Knudsen effusion mass spectrometry
 - Vaporization thermodynamics

- Roth, Robert S.
- Crystal chemistry of ceramic materials
 - Phase equilibria
 - Dielectric and ionic conducting ceramics
 - Phase diagrams for ceramists data center
- Schenck, Peter K.
- Laser spectroscopy
 - Temperature measurement
 - Computer graphics

Structural Chemistry

- Block, Stanley
- Properties, structure and polymorphism of materials at pressure
 - Ultra high pressure properties
 - Crystallography and pressure phase relations of ceramics
 - Generation/measurement of high pressures
- Piermarini, Gasper J.
- Pressure/temperature effects on ceramic materials
 - Generation/measurement of high pressures
 - Physical and structural properties of materials at high pressures and temperatures
 - X-ray diffraction, phase relations, optical measurements

Ceramic Powder Characterization

- Dragoo, Alan L.
- Characterization of ceramic precursor powders
 - Chemical bonds in solids
 - Corrosion of structural ceramics
 - Ceramic powder synthesis
- Hubbard, Camden R.
- Crystallite size and residual stress
 - Quantitative x-ray diffraction methods
 - X-ray diffraction standard reference materials
 - Reference powder patterns (JCPDS Research Associateship)
- Minor, Dennis B.
- Analytical SEM of ceramics and particulates
 - Ceramic composites
 - High temperature ceramic synthesis
- Robbins, Carl R.
- Fine ceramic particulate properties and characterization
 - Spray drying; powder preparation
 - Quantitative microscopy and x-ray diffraction
 - NDE of ceramics

Surface Chemistry and Bioprocesses

- | | |
|-------------------------|---|
| Blair, William R. | <ul style="list-style-type: none">● Ultratrace metals speciation● Biotransformations of metals● Environmental durability of coatings● Molecular surface characterization |
| Brinckman, Frederick E. | <ul style="list-style-type: none">● Organometallic chemistry● Biological mediation of surface chemistry● Ultratrace metal speciation |
| Olson, Gregory | <ul style="list-style-type: none">● Metals biotransformation● Bioprocessing industrial materials● Epifluorescence microscopy imaging● Surface modification and bioadhesion |
| Parks, Edwin J. | <ul style="list-style-type: none">● Metalloorganic synthesis● Macromolecular organometallic chemistry● Metals imaging in coatings● Ultratrace metal speciation● Controlled-release and bioactive polymers |

PROCESSING

Structural Science

- | | |
|----------------------|--|
| Blendell, John | <ul style="list-style-type: none">● Ceramic processing and sintering● Sol-gel chemistry● Diffusion controlled processes● Activation analysis |
| Coblentz, William S. | <ul style="list-style-type: none">● Ceramic processing● Sintering (theory and experiment)● Covalently bonded ceramics● Sol-gel chemistry |
| Fuller, Edwin R. | <ul style="list-style-type: none">● Atomistic models of fracture● Fracture mechanics of ceramics● Fracture, environment-assisted● Mechanical properties at high temperature● Nondestructive evaluation |

Ceramic Chemistry

- | | |
|---------------------|---|
| Coyle, Thomas D. | <ul style="list-style-type: none">● Inorganic and organometallic chemistry● Chemistry of materials processing and durability● Low temperature synthesis of ceramic powders● Chemistry of ceramic precursor materials |
| Frase, Katharine G. | <ul style="list-style-type: none">● Electrical properties● Ceramic powder synthesis and processing● Neutron scattering |

Rhyne, Kay A.

- Ceramic processing
- Small angle neutron scattering
- Nondestructive analysis
- Colloid and sol-gel chemistry

Ritter, Joseph J.

- Synthetic inorganic chemistry
- Ceramic powders from organometallic precursors
- Ceramic powders from gas phase, and solution precipitation reactions

TECHNICAL ACTIVITIES

PROPERTIES/PERFORMANCE

Ceramic materials are used where special properties, such as extreme hardness, chemical resistance to corrosive environments, mechanical resistance to erosion and wear, and mechanical and chemical resistance to temperature extremes, are required. In practical applications, ceramics are used as optical fiber waveguides, substrates for electronic packaging, linings for geothermal wells, components for high-temperature gas turbines and heat exchangers, cutting tools for the shaping and finishing operations used in the manufacture of various machines and tools, and insulating linings for reactors and furnaces in the coal-conversion and petrochemical industries. In defense applications, they are used in radomes, missile nose cones, turbine components in portable electric-generating facilities, electronic guidance systems and bearing surfaces in gyroscopes. Because they are brittle, ceramics are usually over-designed mechanically to avoid fracture during use. Investigations of fracture and deformation properties are needed to overcome technical difficulties associated with this brittle behavior, so that ceramics might be used in a wider range of applications. From a purely scientific standpoint, brittle fracture systems provide fundamental information on the cohesive properties of solids, surface physics and chemistry, and material microstructure.

Our program on mechanical properties has as its broad objectives: (1) the generation of new theories and data to elucidate fracture and deformation mechanisms in brittle materials; (2) the development of new techniques for studying the fracture of and identifying defects in these materials; (3) the collection of engineering data for structural applications; (4) the investigation of processes that result in strength degradation and wear; and (5) the investigation of ceramic microstructure and its relationship to mechanical behavior.

Representative Accomplishments

- o A microstructural dependence of fracture resistance was demonstrated in polycrystalline ceramics using the controlled flaw technique. Below a critical flaw size, the strength was found to be independent of flaw size for a number of ceramics. This behavior differs from the classical Griffith behavior, suggesting that the resistance to fracture increases as the cracks grow larger. Because of these results, methods of material characterization for lifetime prediction will have to be modified to account for rising resistance curves for fracture of ceramic materials.
- o A new theory to explain fracture toughness of ceramic materials was developed. The source of the toughness of ceramic materials is believed to originate in interlocking grains and unbroken ligaments that cross between the crack faces. These apply a closure force to the crack that must be overcome for fracture to proceed. This theory implies that the toughness of ceramic materials can be enhanced by microstructural design to increase the degree of interlocking of fracture surfaces. Studies have shown that this mechanism of toughening is applicable also at high temperature.

- o The role of surface forces in subcritical crack growth was explored for ceramic materials. The equation developed to characterize the effect of surface forces on crack growth suggests that surface forces can account for a number of physical observations including the healing of ceramics when the external driving forces are removed, the change in slope of crack growth curves when the external environments are changed, and the presence of fatigue limits in ceramic materials. These theoretical predictions are being investigated through experimental studies on mica and on glass.
- o A study of creep in bending demonstrated that the neutral axis for strain moves from the geometric center of the bend specimen toward the compressive surface as the strain increases. Data of this type are being collected to confirm predictions of theories of multi-axis creep. These results suggest that creep measurements obtained by both tensile and compressive techniques are needed to understand fully the creep of ceramic materials in high temperature applications.
- o An analysis of the creep rupture of vitreous bonded aluminum oxide indicates that failure of ceramic materials at high temperatures can be divided into stress and strain limited modes, the latter being more important for long term structural applications. These results support data obtained on other structural materials such as hot pressed silicon nitride and hot pressed aluminum oxide. They imply that fixed strain relationships of lifetime prediction such as the Monkman-Grant relationship will be more relevant at elevated temperatures than fracture mechanics derived relationships.

Contact Damage and Flaw Studies

B.R. Lawn, C.J. Fairbanks, D.E. Roberts, B.J. Hockey, Y.-W. Mai¹ and R.F. Cook²

¹ Guest Worker, University of Sydney

² Guest Worker, University of New South Wales

Contact damage studies using indentation methods provide valuable insight into the fundamental deformation and fracture properties of materials. They are now used widely in the ceramics community (perhaps more than any other technique) as a means for evaluating critical material fracture properties. They are used for determining surface stresses in high-strength ceramics; as a basis for modelling wear, erosion, and machining properties of brittle materials; in the design of ceramic components for potential strength-degrading applications; and as model flaw systems in order to study the underlying the physical and chemical processes that are responsible for the initiation of small cracks. As such, contact damage techniques afford a powerful route to the systematic study of the micromechanics of small flaws, which control the strength of ceramics.

During the past year the effect of contact damage on the strength and static fatigue behavior of a number of ceramic materials was studied. For documentation of the propagation of cracks from indentation sites, discs containing one indentation each in their center were placed on a test fixture that was mounted on an inverted optical microscope. Loads applied to the specimens caused the cracks to grow, and the crack growth was

recorded on a video tape recorder so that the qualitative aspects of crack growth could be documented. Crack growth did not occur in a continuous fashion but in incremental steps. Fracture was often interrupted at one point only to restart at a second, nearby point. These results suggest that interlocking grains and ligaments of unbroken material in the wake of the crack front served to apply a closure force to the crack surface which must be overcome for the crack to propagate. Based on the above observations, a model of crack growth has been developed that derives its resistance to crack growth from the unbroken ligaments in the wake of the crack front. This model has been used to obtain a prediction of strength and failure time as a function of microstructure. The predictions are currently being tested in stress rupture studies at room temperature. The output of this project is expected to suggest changes in current methods of design for ceramic materials.

Chemically Effects in Crack Growth and Healing

D.H. Roach, B.R. Lawn and D.E. Roberts

The objective of this portion of our work is to understand the mechanisms by which a chemical environment can enhance crack growth rates in glasses and ceramics. Our present state of understanding of chemically enhanced fracture is primitive in the sense that while we can measure crack growth or strength degradation rates, our lack of knowledge of specific mechanisms prevents us from selecting materials that have a maximum resistance to crack growth. This same lack of knowledge prevents us from applying fracture mechanics theory to predict component lifetimes that extend much beyond the time range of the experimental data. Our research program is a means of obtaining this knowledge.

During the past year a study was conducted to determine the effect of surface forces on crack growth in glass and mica at room temperature. Fracture mechanics techniques were used to study crack growth and crack healing in a number of environments: air, water, and aqueous electrolytes. Crack growth studies of healed fractures indicate a strength increase with time; however the strength never reaches that of the original material. The healing process is believed to originate from surface forces whose origins are probably of a chemical nature. Mathematical analyses of the type of behavior expected from such forces are consistent with experimental observations: the occurrence of crack healing, the observation of threshold effects during fracture and the dependence of crack growth on environment. Experimental studies and theoretical modeling during the coming year are expected to improve our understanding of the effect of surface forces on the fracture of ceramic materials.

Flaw Propagation and Microstructural Effects

B.R. Lawn, A.C. Gonzalez, C.J. Fairbanks, D.E. Roberts and R.F. Cook¹

¹Guest Worker, University of New South Wales

Because the crack propagation resistance of ceramics is relatively low, critical flaw sizes are reduced to a level at which they can become comparable to the size of microstructural features (typically 5-50 μm).

This comparability of flaw and grain sizes can lead to additional driving and resistance forces on small-scale cracks, e.g., due to thermal expansion anisotropy. It can also lead to an increase in the intrinsic toughness, as a result of crack deflection processes, as fracture proceeds. An understanding of the mechanisms of crack-microstructure interactions, and the implications of these phenomena in relation to design with ceramics, are the objectives of our work in this area.

The controlled flaw technique is an ideal method of studying the dependence of fracture resistance on flaw size. Indentation flaws are placed into polished surfaces of ceramic materials, and strength is measured as a function of flaw size. In conducting a study of this type, we found the strength to be highly dependent on the microstructure of the ceramic. For some ceramics the strength was independent of crack size below a threshold size crack. For others, the strength followed a classical brittle behavior in which the strength is inversely proportional to the square root of the crack size. These results can be explained by a crack size dependence of the toughness of the material. Resistance to crack growth increases as the crack grows larger so that the crack propagates in a stable fashion, until it reaches a critical size determined by the microstructure and the crack geometry. Thus, whether the crack is small or large, specimens fail at the same breaking stress. The existence of a rising resistance curve for fracture suggests that microstructure is important to the lifetime and strength of ceramic materials, and as such can be modified to improve the fracture behavior. Because of the importance of a rising fracture resistance to strength, additional studies will be conducted during the coming year to fully evaluate the role of microstructure on toughness.

High-Temperature Deformation and Fracture

S.M. Wiederhorn, E.R. Fuller, Jr., T.-J. Chuang, N.J. Tighe, R.F. Krause, Jr., B.J. Hockey, C.L. McDaniel, L. Chuck, G.A. Danko, Y. Lu¹, and J. Sun²

¹Shanghai Institute of Testing Technology, Shanghai, China

²Shanghai Institute of Ceramics, Shanghai, China

The development of new ceramics provides hope for high efficiency, enhanced performance of structural systems in high temperature, stress-bearing environments. However, before ceramics can be used in industrial applications, issues concerning reliability and service life remain to be resolved. With this in mind, our program on high-temperature properties of ceramics entails five objectives: (i) the development of new theories that are capable of predicting time-dependent fracture and deformation behavior at specified loads and temperature; (ii) the development of new experimental techniques that can produce reliable creep data; (iii) the generation of a data base on commercially available ceramics and refractories; (iv) the investigation of kinetic processes that result in strength degradation and delayed failure; and (v) the examination of microstructures that promote understanding of mechanisms of response to creep and creep rupture.

High temperature fracture studies during the past year concentrated on four materials: partially stabilized zirconium oxide, magnesium chromate refractory, siliconized silicon carbide, and aluminum oxide. In all of these studies the strength or creep behavior was characterized as a function of temperature, time, and load.

Studies on partially stabilized zirconium oxide, a candidate for diesel engines, indicate little loss of strength at temperatures up to 1000 °C for exposure times of approximately 500 hours. At 1000 °C, a slight increase of strength is observed as a function of time at temperature, followed by a strength decrease after extended periods of loading. Since the material creeps readily at 1000 °C, studies indicate the occurrence of stress induced flaw generation as a function of creep, which eventually causes the specimen to fracture. At 1000 °C the monoclinic phase grows at grain boundaries at the expense of the tetragonal phase, and also contributes to the strength loss. After exposure, the strength was highest at room temperature for all test conditions. Toughness tests on this ceramic show a very high insensitivity to damage; flaws up to approximately 80 μm do not affect room temperature strength at all.

Magnesium chromate refractories are used as liners of slagging coal gasifiers. Efficient operation of these gasifiers is required to produce gas at a reasonable cost for commercial utilization, which implies high temperatures of operation > 1500 °C. Present gasifiers are limited to approximately 1500 °C because of chemical instability of the refractory and the sensitivity of the refractory to creep rupture. In this project the creep rupture of magnesium chromate refractory is being quantified to correlate mechanical properties with failure mechanisms. Last year, the creep rupture of as-received material was characterized as a function of temperature and stress. The creep curves exhibited work hardening behavior and the strain could be fitted to a power law function of the time, in which the exponents and coefficients of the fit were both stress- and temperature-dependent. The strain rate data were found to fit the empirically derived expression to better than 5 percent of the strain rate. The equations developed will be used in other parts of the program to establish engineering allowables for coal gasification liners.

Creep-rupture studies of siliconized silicon carbide were conducted because of the potential use of this material in heat exchangers. At the maximum temperature of use of this composite, silicon is a highly ductile metal, whereas silicon carbide is a completely rigid solid so that creep of the composite therefore depends on the rheology of the silicon and the way in which the silicon carbide affects the rheology of the silicon. Flow of the silicon between the grains of silicon carbide accommodates the deformation, but when the silicon cannot flow rapidly enough, cavitation occurs. Cavitation and the growth and linkage of cavities to form cracks are the main microstructural processes that limit the lifetime and strength of this composite. During the past year, the creep and creep-rupture behavior of siliconized-silicon carbide were characterized in four-point bending as a function of temperature and stress. It was shown that cavitation nucleates early in the creep process from preexisting grain boundary defects. With additional deformation, the nucleation and growth of defects continues, eventually resulting in large cracks that lead to failure. As a consequence of the cavitation, the neutral strain axis for bending shifts towards the compressive surface of

the test specimen. A method has been developed for locating the position of zero strain and will be used to collect data that can be compared with theoretical treatments of multi-axis creep.

The nucleation and growth of cracks at elevated temperatures was studied on a commercial grade of vitreous bonded aluminum oxide by flexural loading. This material was selected because it contained glass at the grain boundaries and could be used as a model for structural materials that are glass bonded. The strength of this material at elevated temperatures was insensitive to the damage accumulated by the creep process, suggesting a rising resistance curve for crack growth as the crack grows from a subcritical to a critical size. This interpretation is supported by the observation of ligaments of unbroken material along the surfaces of propagating cracks. As in the case of our studies at room temperature, these ligaments increase the toughness of the material by applying a closure force to the crack surfaces. Since cracks nucleate along clusters of grain boundaries, deformation is believed to be heterogeneous in this material. Creep-rupture data are shown to fit a stress-modified Monkman-Grant plot which suggests that a finite amount of deformation is required in this material for the occurrence of failure. Consistent with this conclusion is the observation that a relatively fixed amount of strain is required in order to nucleate cracks in this material.

The Glass and Composite Group performs research in a number of areas with a strong emphasis on the mechanical properties of glasses, polycrystalline ceramics, and ceramic matrix composites. In particular, there are major efforts in the study of environmentally enhanced crack growth in brittle materials, effects of ceramic microstructure on crack growth, and development of fracture testing procedures applicable to ceramic matrix composites. In this regard, there are cooperative efforts with personnel in both the Mechanical Properties Group and the Processing Group within the Ceramics Division. There is also a considerable effort being placed in the development of non-destructive evaluation (NDE) procedures for ceramics and ceramic composites with emphasis on thermal wave analysis. In addition, there is ongoing work related to the development of glasses that can be used for x-ray fluorescence standards. The Glass and Composite Group is also involved in the determination of glass viscosity over a wide range in temperatures. This latter work is important from the point of view of glass viscosity standards. In addition viscosity is one of the key parameters which determines the creep behavior of polycrystalline ceramics that have glassy grain boundary phases.

Representative Accomplishments

- o Work on understanding the mechanism of stress enhanced chemical reactions at crack tips has been extended from oxides to materials such as III-V and II-VI compounds, e.g., GaAs, ZnSe, having variations in their ratio of covalent to ionic bonding. Preliminary indentation crack length procedures have shown that the fracture energy of these compounds decreases with increasing ionicity of the chemical bond.
- o Thermal wave techniques for porosity have been successfully applied to alumina.
- o Two new glass SRM's have been developed for calibration of x-ray fluorescence spectrometers.

Reactions at Crack Tips

Stephen W. Freiman and Grady S. White

Calculations of fracture energies based on a relatively simplistic model agree very well with the experimental measurements. All of the materials investigated, except for silicon, showed environmentally enhanced crack growth in water. There is evidence that chemical compounds such as acetonitrile, which does not cause crack growth in SiO_2 in preference to water, are much more effective in a stress enhanced crack tip reaction in the case of more ionic materials such as MgF_2 and ZnS . No environment was found to produce slow crack growth in Si.

Microstructure/Crack Interaction

Stephen W. Freiman, Theresa L. Baker and Peter L. Swanson

Indentation-fracture procedures have been used to determine effects of starting powder and processing conditions on the fracture behavior of a 94 percent alumina. It was found that both the critical fracture toughness and the strength of the aluminas were sensitive to the starting powder but not to variations in sintering conditions. Deviations of the strength from that predicted by the indentation model for small flaws were ascribed to direct effects of the microstructure, possibly due to stresses generated by the thermal expansion anisotropy in the material. The stress corrosion susceptibility of the alumina was shown to be highly sensitive to the starting powder, but again relatively insensitive to sintering conditions. Differences in the subcritical crack growth behavior have been hypothesized to be due to differences in the grain boundary compositions which have been shown to differ markedly in their MgO/SiO₂ and CaO/SiO₂ ratios for the two starting powders investigated to date.

Glass SRM's

Douglas Blackburn and Dale A. Kauffman

In cooperation with the Center for Analytical Chemistry, two thin film Standard Reference Materials, SRM 1832 and 1833 have been developed and issued for the calibration of x-ray fluorescence spectrometers. Each SRM consists of a silica-base glass film deposited by focused ion beam coating onto a polycarbonate substrate. The film consists of an amorphous glass layer 0.5 - 0.6 μm thick containing known concentrations of selected elements in oxide form. SRM 1832 is certified for Al, Si, Ca, U, Mn, Co and Cu, and SRM 1833 for Si, K, Ti, Fe, Zn and Pb. Further work is in progress for the development and certification of SRM's containing Si, B, Li, Pb, Sn, Cd, Sb and Cr in one glass composition and Si, Al, Ba, Na, Ni, Mo, AS and Cd in another glass. An ion sputtered arsenic sulfide glass film shows considerable promise as a sulfur standard, and is surprisingly stable and durable.

Thermal Wave NDE

Grady S. White, Loretta A. Inglehart and Martin P. Jones

The major NDE thermal wave effort for this year involves the measurement of porosity in alumina specimens. The photo acoustic system built last year has been used to obtain preliminary signal magnitude and phase data on NBS prepared alumina specimens, which are 58 percent, 60 percent, and 98 percent of theoretical density. Clear differences in both magnitude and phase are observed among all three specimens. In addition to the thermal wave measurements, the alumina is also being characterized by a number of other techniques, e.g., light scattering, small angle neutron scattering (SANS), porosimetry, and ultrasound, to provide as thorough an understanding of their properties as possible. Such an understanding is vital to the development of a quantitative model relating thermal waves to the measurement of porosity.

In addition, a mirage thermal wave system is being built at NBS to provide imaging capabilities. The mirage system is designed to be computer controlled and will allow detection and mapping of closed vertical cracks, inclusions, and other localized defects.

The wear of solid materials is one of the more pervasive cost factors that affects every industrial, government, and civilian element in our society. Tribology is that part of science that addresses the problems of wear and the related problems of friction and lubrication.

The emergence of tribology as a distinct interdisciplinary field of study has resulted from the recognition that the physical, chemical, and material aspects of interacting substances are all crucial concerns of friction, wear, and lubrication. The effects of these various aspects are coupled together; i.e., the physical, chemical, and material aspects must be considered at the same time.

The Tribology Group has developed a strong chemistry component to study tribological interactions, particularly as they are mediated by a lubricating medium. Special emphasis in this work has been placed on the very important regime known as boundary lubrication.

The subject matter of tribology is also prominent in current efforts to develop materials for high temperature applications such as low heat rejection engines. Advanced ceramics are the most promising candidate materials for such purposes. However, at the expected high temperatures (600 °C in the near future; 1200 °C in the distant future), traditional lubrication substances and methods are not feasible. Similarly, common performance measurement approaches used to determine friction and wear characteristics are not feasible at high temperature.

Representative Accomplishments

- A unique new facility has been designed to study the friction and wear properties of ceramic materials at high temperatures. The principal apparatus is capable of simulating the wear of both piston and ring and cam and tappet engine component combinations. The environment of the sample region has a controlled temperature which may be as high as 1500 °C. The atmosphere is also controlled allowing for studies in oxidizing and nonoxidizing environments and for studies of novel lubrication methods such as the chemical vapor deposition technique.
- A novel simulation method has been developed for prediction of lubricant performance at high temperature. The method is based on thermogravimetric analysis, a technique that uses a highly sensitive mass balance to detect variations in the mass of a milligram size sample as a function of time and temperature. Successive experiments using inert and oxidative environments permit thermal and oxidative characteristics to be measured. Difference curves and derivatives of the weight loss curves are related to the molecular weight change of the chemical species during the oxidation process. Relative comparisons of the integrated areas under the difference curves and the derivative curves reveal quantitative information on the amount of interfacial reaction products as well as the oxidative influence on evaporation under thin film liquid/solid interface reaction conditions. This simulates the heat engine cylinder liner/ring interaction.

Lubrication

P. Pei, R. S. Gates, C. S. Ku, K. L. Jewett, and R. G. Munro

Lubricating materials in tribological contacts react chemically with the substrate material to form a surface film that is largely responsible for the success of boundary lubrication. The efforts of this Group have contributed significantly to the advancement of lubrication fundamentals.

Important steps have been made in resolving the very long-standing question of what in a lubricating base oil actually is responsible for the lubricant's effectiveness. The question was attacked in two phases. First, a highly sophisticated base oil separation methodology was developed to study molecular structural effects. The base oil was separated into its saturate, aromatic, and polar fractions; and subsequently the polar fractions were further separated into subfractions and then into compound classes.

Second, the separated substances were subjected to a variety of tests to measure: oxidation stability; lubricating film formation tendencies; and friction and wear performance characteristics. Subsequently, spectroscopic studies were made on the most successful materials.

From these studies, model compounds were identified that would be representative of the substances producing the superior friction and wear characteristics. Performance tests conducted on the model compounds γ -butyrolactone and myristoyl chloride confirmed the deductions based on the spectroscopic analysis. The insights into lubrication fundamentals provided by this effort could well require several years before being fully appreciated because of the multitude of subtle features uncovered by the study.

Ceramics Tribology

R. S. Gates, J. P. Yellets, D. E. Deckman, and R. G. Munro

High technology ceramic materials have a tremendous potential for applications as structural materials. This potential for ceramics derives from their outstanding thermal characteristics, high corrosive resistance, and dimensional stability. The principal challenges in the development of these materials are related to the strength, durability, and wear resistance of the materials. An integral part of the design and advancement of these ceramics applications, therefore, is the performance testing and characterization of the materials. Currently, however, there are no standardized test methods for evaluating the tribological properties of ceramics.

The Tribology Group has initiated a program in the tribology of high temperature ceramics. The program involves the development of standardized methodologies for friction and wear measurements; the simulation of engine component wear at high temperature; and the lubrication means and methods for ceramic materials at high temperatures.

In the past, several wear test procedures have been successfully developed at NBS for lubricated steel system. One of these procedures has been selected by ASTM for consideration as a standard method for determining coefficient of friction. The method established for lubricated steel systems has considered carefully the importance of material properties; wear test geometry; load, speed, and temperature parameters; and systematic pre- and post-test procedures.

The material properties of ceramics, however, are significantly different from those of steel, to such an extent that entirely new detailed procedures are required. Some intriguing and novel features in ceramics friction and wear tests are now being discovered. These features will require incorporation into any standardized methodology for ceramics friction and wear measurement procedures.

Temperature effects have been found to be especially important for ceramic wear processes. Figure 1 shows the coefficient of friction (COF) for polycrystalline alumina under three different conditions, dry or lubricated with paraffin oil or with water. The COF with water lubrication is greater than the COF with paraffin oil. Thus, the heat generation rate in the former case should exceed that of the latter case. Water, however, is a much better coolant than paraffin oil. Consequently, the temperature under water lubrication tends to be lower than under paraffin oil. The result of having a lower temperature is illustrated by Figure 2 which shows a measure of the wear of the alumina specimens. The coolest system has the lowest wear, despite not having the lowest friction. The hottest system has the highest wear.

Additional considerations arise for the testing of ceramic materials at very high temperatures. The low thermal conductivity and thermal diffusivity of ceramics results in the generation of very high temperatures in tribological contacts. Estimates of peak temperatures at surface asperities have been as high as 2000 °C. Cooling occurs as the hot parts move away from the contact zone. Consequently, large temperature gradients normally are produced in standard test apparatus. These gradients obscure the understanding of the intrinsic friction and wear properties. Therefore, the Tribology Group has designed a new wear test apparatus for ceramic materials with the principal feature being the minimization of large temperature gradients around the contact zone.

The new facility features control of the temperature to 1500 °C, control of the local atmosphere, and a sophisticated data acquisition, storage, and retrieval system. The facility is expected to be fully operational early in FY86, dependent on the delivery of unique and specially designed components.

The use of ceramic materials at high temperature also poses a very significant challenge to lubrication techniques. One methodology which provides a means for accessing the suitability of materials for high temperature lubricating applications is thermogravimetric analysis. In a high temperature environment, lubricants are susceptible to numerous reactions including oxidation and thermal stability. In heat engine applications, high vapor pressure and oxidative volatility cause excess lubricant loss through oil consumption. On the other hand, amount of deposit formation on metal

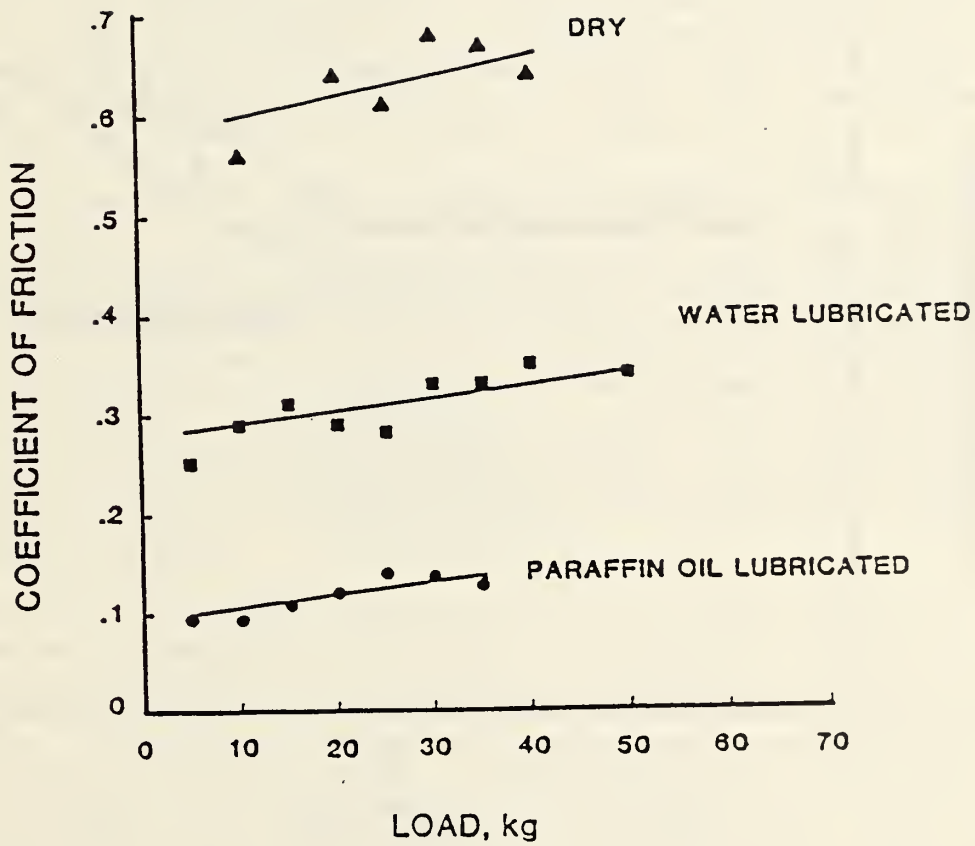


Figure 1 . Coefficient of Friction as a function of Load for Polycrystalline Alumina from Four-Ball Constant Condition Tests Conducted at 600 rpm, 10 min duration, 10 ml lubricant.

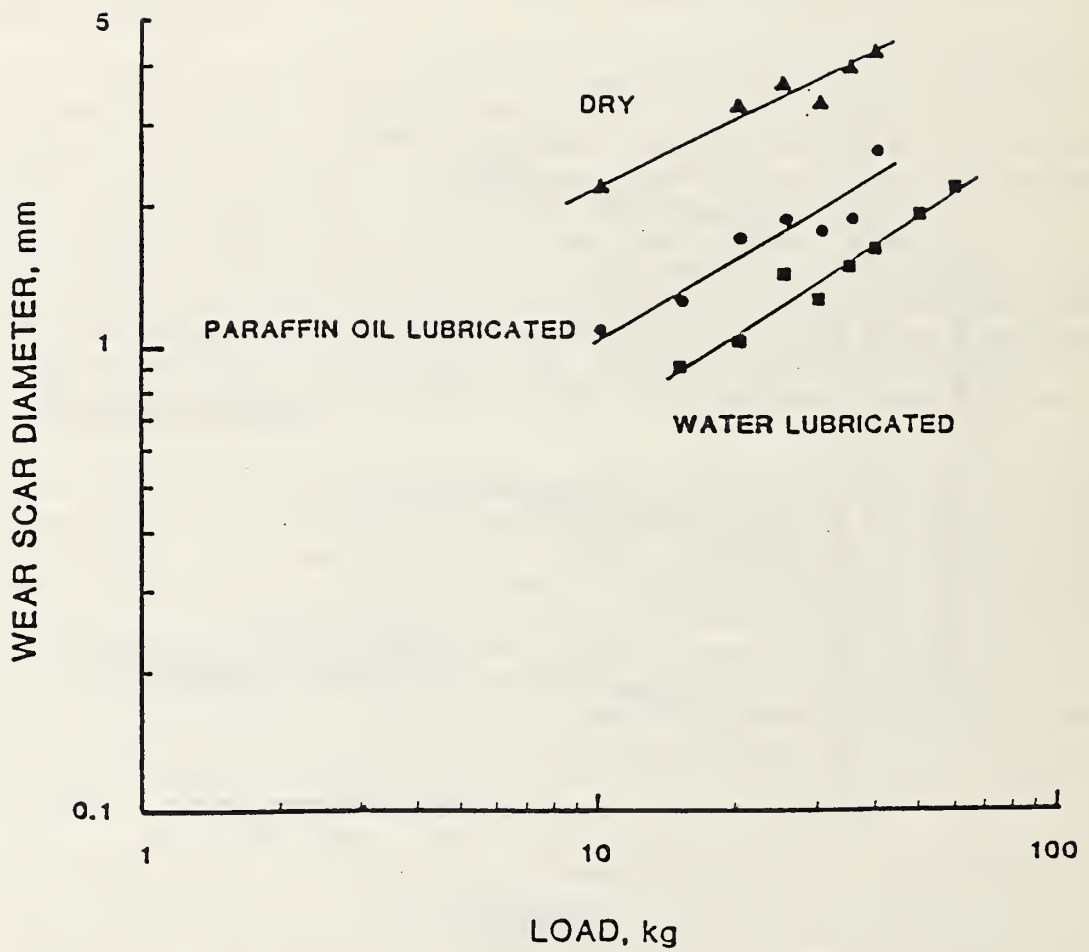


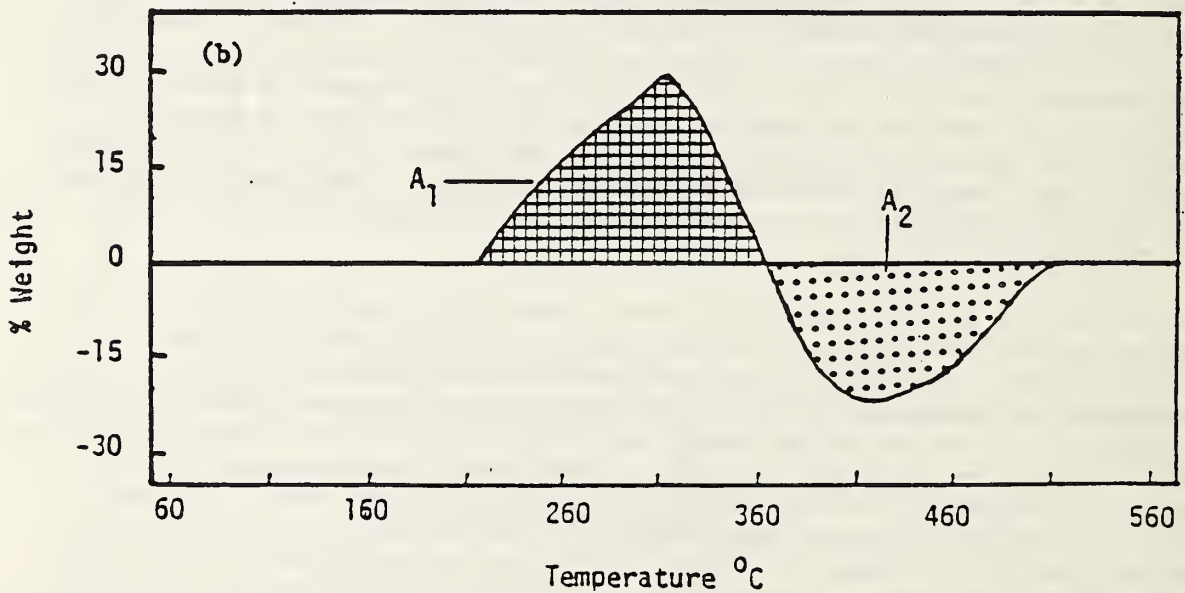
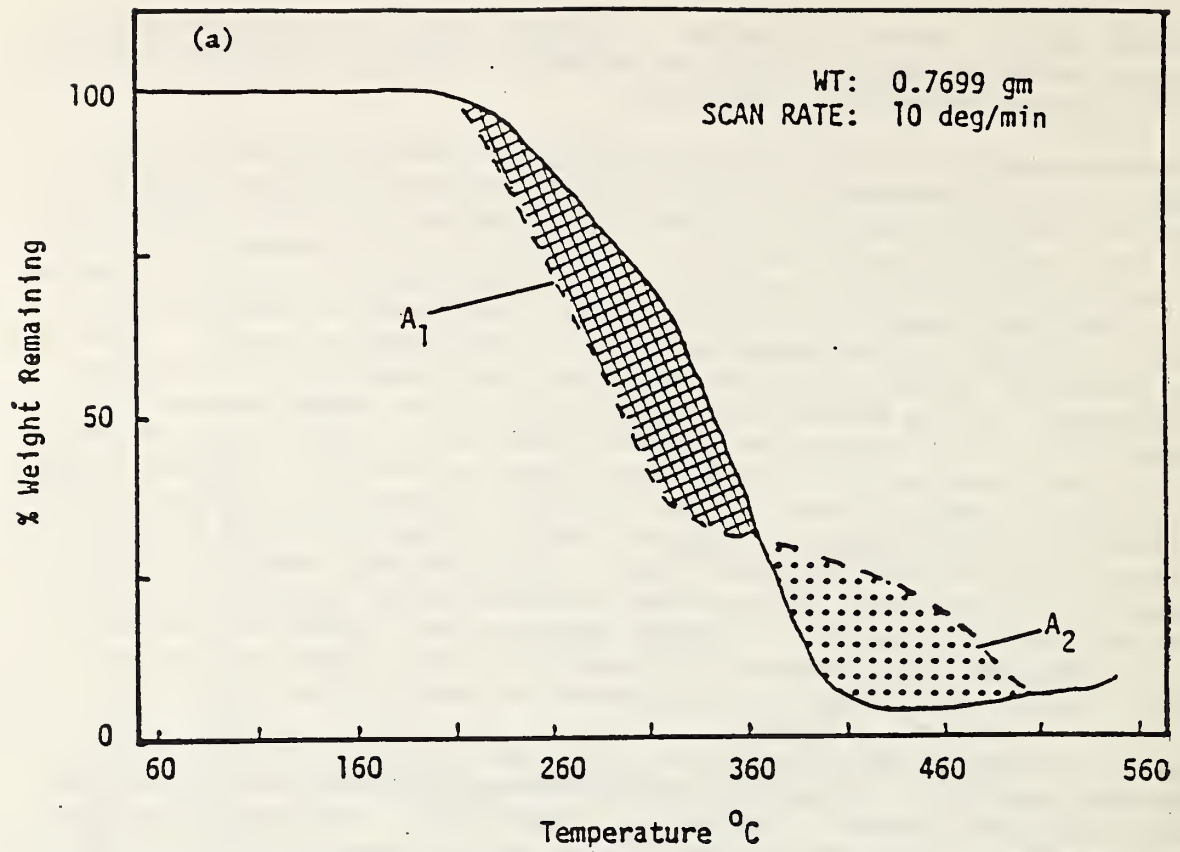
Figure 2 . Wear as a Function of Load for Polycrystalline Alumina from Four-Ball Constant Condition Tests Conducted at 600 rpm, 10 min duration, 10 ml lubricant.

surfaces is also crucial in engines. Thermogravimetric analysis provides a means of assessing the volatility and oxidative stability characteristics of potential high temperature lubricants.

A thermogravimetric method has been developed to assess candidate lubricants. In this procedure, 0.7 to 0.8 mg of lubricant is placed on a steel catalyst disk contained within a gold pan. The sample is then heated at a rate of 10 deg/min from 50 to 550 °C. As the sample is heated, the percent of sample remaining within the pan is monitored. After the sample is heated in an argon environment, the catalyst disk is replaced, a fresh lubricant sample is added, and the sample is heated in an oxygen atmosphere. Figure 3(a) shows the thermal and oxidative weight loss curves for an alkylated naphthalene. In the thermal test 100 percent of the sample remains until roughly 210 °C when evaporation becomes significant. Eventually, complete evaporation occurs and no further weight loss is observed. Under an oxygen environment, primary oxidation occurs forming decomposition products with greater volatilities than the original sample. These molecules evaporate at a faster rate than in the thermal case. Simultaneously, some of the primary oxidation products react to form high molecular weight species which are less volatile and evaporate at higher temperatures. Therefore, the oxidative weight loss curve eventually crosses the thermal curve and remains above it until all products are evaporated as shown in Figure 3(a).

This new thermogravimetric method provides much critical information on lubricant stability. Subtraction of the two weight loss curves yields the difference curve, which is displayed in Figure 3(b). The areas under the peaks provide a quantitative comparison of relative oxidative volatility and high molecular weight deposit formation tendencies of different lubricants. The ratio of the two areas of a particular lubricant provides information on the potential problem area of volatility rate with respect to deposit formation rate. If area A_1 is much larger than A_2 , then oxidative volatility could be the critical shortcoming for the lubricant. If A_2 is much larger than A_1 , then deposit formation may be the problem. When several lubricants are compared, the relative oxidative volatility characteristics can be quantitatively compared.

The derivative of the weight loss curve results in a weight loss distribution curve for the lubricant in the respective atmosphere on a steel catalyst disk. The weight loss distribution curve obtained for the argon atmosphere is equivalent to the boiling point distribution curve obtained by distillation. The molecular weight distribution determined from the boiling points of various molecular species is consistent with the distribution analysis obtainable from gel permeation chromatography (GPC). The area under the derivative curve equals normalized mass (m/m_0), where m_0 is the initial mass of the sample. Figure 4 displays the negative of the derivative weight loss curve. Region 1 shows low molecular weight species formed during oxidation and region 2 shows high molecular weight species formed by oxidation. The area under the oxidation curve shows the total mass of the oxidized products.



Figures 3(a) and 3(b).

Thermogravimetric Data Obtained from the Analysis of an Alky Naphthalene Mixture: (a) Thermal weight loss curve (----), and oxidative weight loss curve (----); and (b) computer (thermal-oxidative) difference curve.

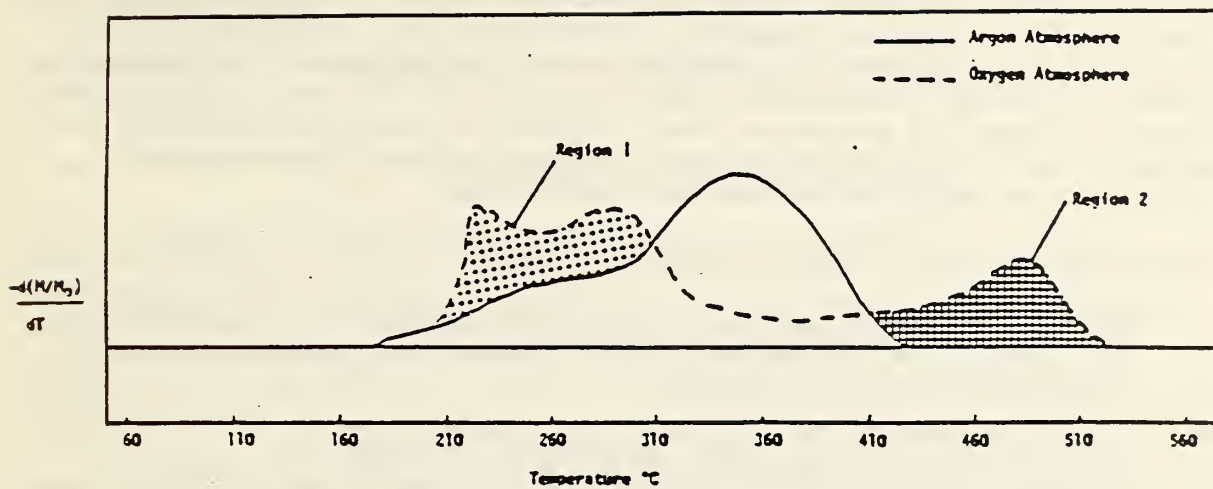


Figure 4. TGA Derivative Weight Loss Curve for an Alkylated Naphthalene in Argon and Oxygen.

The objective of the Optical Properties Group is to provide data, measurement methods, standards and reference materials, concepts, evaluated data, and other technical information on the fundamental aspects of processing, structure, properties and performance of optical materials for industry, government agencies, universities, and other scientific organizations. The program supports generic technologies in crystalline, glassy, and thin film inorganic optical materials in order to foster their safe, efficient and economical use. Research in the group addresses the science base underlying new advanced optical materials technologies together with associated measurement methodology.

Two principal areas of optical materials research are being covered:

Thin optical films addresses structure/processing relationships and how they affect properties and performance as related to optical coatings and integrated optics.

Materials for optical signal processing addresses structure/processing relationships of crystalline electro-optical materials important as modulator and optical memory materials.

In addition to the principal areas of activity, the group maintains the capability to measure refractive index, thermo-optic constants and piezo-optic constants of optical materials.

Representative Accomplishments

- A Topical Conference on Basic Properties of Optical Materials was held at NBS May 7-9, 1985. It was sponsored by the National Bureau of Standards (NBS), the American Physical Society (APS), the Air Force Office of Scientific Research (AFOSR), the Office of Naval Research (ONR), the Army Research Office (ARO), in cooperation with the Optical Society of America (OSA) and the Society for Photooptical Instrumentation Engineers (SPIE). The 17 invited and 53 contributed papers covered basic properties of materials as they affect performance in advanced optical applications.
- Thin films in the zirconia:silica system prepared by coevaporation showed significant densification compared to pure films of zirconia. A simple model was used to estimate the pore fraction of films as a function of composition.
- Quantitative the Electron Spectroscopy for Chemical Analysis (ESCA) measurements showed that coevaporated zirconia:silica films prepared without backfilling with oxygen were significantly oxygen deficient. The results correlated qualitatively with the presence of optical absorption in the films. Pure zirconia and pure silica films were stoichiometric.

- Monochromatic x-ray topography experiments were carried out at the National Synchrotron Light Source. Growth dependent defect structures were observed in high quality single crystals of lithium niobate and bismuth silicon oxide. These are the first such experiments carried out in this country.

Thin Optical Films

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Optical films of zirconia have been receiving considerable attention because of their use as the high-index layer in multilayer optical coatings for the ultraviolet portion of the spectrum. Several problems are associated with electron-beam deposited zirconia films, and these include index inhomogeneity. The index instability is caused by the adsorption and desorption of water in the porous columnar structure of the zirconia films. Index inhomogeneity is due to the inhomogeneous structure of the films. One approach for producing bulk-like zirconia films that is receiving considerable attention at present is ion-assisted electron-beam deposition. We have demonstrated similar results when mixed zirconia:silica films are produced by coevaporation from independent electron-beam sources.

In most of the results discussed below two sets of films were used. The initial set, prepared in a prior year, relied on manual control of the deposition rate. The second set of films, prepared this year, were deposited with the use of automatic deposition rate controllers.

Last year, based on channel spectra and stylus measurements of the thickness (t), we reported that a small addition of silica to zirconia produces a film possessing a higher refractive index (n) than a pure zirconia film. These results have been confirmed both by additional independent measurements of n and t on the same set of specimens by m -line spectroscopy, and by channel spectra and stylus measurements on a larger number of the new second set of specimens. We have now shown that this anomolous index behavior is consistent with a decrease of porosity in the mixed films with the increasing content of silica. This result is based on thickness measurements which show that the sum of the individually monitored thicknesses of the two components is always less than the measured thickness of the film.

If we define a nominal densification as a ratio of the sum of monitored thickness to the measured film thickness, we find a densification of all mixed films when compared to pure films of zirconia and silica. A simple model has been used to estimate the porosity of mixed zirconia:silica films as a function of composition. The porosity deduced for pure zirconia films is estimated to be 25-40 percent depending on the manner of deposition. This is consistent with porosities estimated from our measurements of the effect water adsorption on refractive index and with values reported in the literature. In addition, the mixed films appear to exhibit a greater index stability than the pure zirconia films.

The effect of composition on the stoichiometry of e-beam coevaporated zirconia:silica films was obtained by quantitative ESCA measurements. Measurements of the area under the O_{1s} , Zr_{3d} , Si_{2p} ESCA peaks yielded the atomic fractions of O, Zr, and Si. The films about 100 nm thick of varying composition were deposited without backfilling with oxygen. After preparation, the films were transferred directly to the analytic chamber without breaking vacuum, thus avoiding specimen contamination. The pure zirconia and silica films appeared to be stoichiometric. However, all the mixed films exhibited oxygen deficiencies with the film having a 50:50 ratio of zirconia to silica being the most oxygen deficient. We are planning to determine whether backfilling with oxygen will lead to more stoichiometric coevaporated films.

These results correlate with the visual appearance of the new set of specimens discussed above. Those films showed a significant optical density with compositions closest to a 50:50 ratio having the darkest appearance. Upon bakeout in air at temperatures ranging from 400-600 °C, the films became fully transparent, with the most optically dense films requiring the highest temperature.

Rutherford backscattering (RBS) experiments were made on the first set specimens discussed above to examine depth uniformity. Looking at the Zr signal, we found good uniformity at low silica composition, however, the nonuniformity increased significantly with increasing fraction of silica.

OM85, Topical Conference on Basic Properties of Optical Materials

A Topical Conference on Basic Properties of Optical Materials was held at NBS May 7-9, 1985. It was sponsored by NBS, The American Physical Society, The Air Force Office of Scientific Research, the Office of Naval Research, and the Army Research Office in cooperation with the Optical Society of America and SPIE-the International Society for Optical Engineering. A total of 204 people registered for the conference.

The purpose of the conference was to bring together researchers from industry, academia, and government to discuss the physical and structural properties of optical materials as they affect performance. The principal topical areas covered were Effects of Microstructure, Infrared Materials, Organic Materials and Polymers, Waveguide Materials, Surface Plasmons, Thin Films, Properties from Millimeter to X-ray Wavelengths, Semiconductors and Quantum Well Structures, Nonlinear Optical Materials, Optical Bistability and Glasses. There were 17 invited papers and 53 contributed papers.

Materials for Optical Signal Processing

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Activities in materials for optical signal processing are focussed on both optically passive and active materials.

In the active materials area, initial monochromatic topographic experiments have been carried out during the first period of dedicated beam operation of the x-ray ring at the National Synchrotron Light Source. Samples of lithium niobate grown under a variety of conditions and of bismuth silicon oxide were observed to display highly growth-dependent crystal structure. We are working closely with industrial and university crystal growers to identify the specific sources of crystal variation. Parallel chemical analysis experiments are being carried out with neutron depth profiling techniques at the Bureau's research reactor.

STRUCTURE/STABILITY

Our program in high temperature chemistry and phase equilibria emphasises the structural, thermodynamic, and chemical-kinetic behavior of materials in high-temperature/high-pressure (gaseous) process and service environments. Phase equilibria, crystal structure, and reaction mechanisms of ceramic and glass systems are determined through modeling and experiment. The Phase Diagrams for Ceramists Data Center compiles and evaluates ceramic phase diagrams in cooperation with the American Ceramic Society.

This activity serves new technologies, such as those based on processing of advanced ceramics, refractory ceramic durability, nuclear waste management, electronic ceramics, and more efficient fossil fuel combustion. Industry and other government agencies use the results (a) for performance predictions and test method development in new high technology applications, and (b) to support materials processing at high temperatures.

The research addresses: development of new or improved experimental methods, their application to determination of basic data and new concepts, modeling of ceramic/metal gas-liquid-solid equilibria, and critical evaluation and compilation of ceramic phase equilibrium diagrams. Molecular-specific experimental methodologies and theoretical modeling tools are also being developed and applied to the determination of basic thermochemical and kinetic data and chemical reaction mechanisms. In support of phase diagram determinations, and for the completion of thermodynamic cycles in gas-solid-liquid equilibria, the characterization of condensed phase composition and structure is achieved by x-ray or neutron diffraction, scanning and transmission electron microscopy, and electron spectroscopy for chemical analysis (ESCA).

During the past year, six inter-related subtasks have been carried out: (1) Phase Diagrams for Ceramists Data Center; (2) Phase Equilibria and Structural Chemistry; (3) High Temperature Chemistry; (4) Characterization of High Temperature Gaseous Environments in Processing and Service; (5) Data Center on Materials and Components for Fossil Energy Applications; and (6) High Temperature Thermophysical Properties. The following discussion will highlight the first three areas.

Representative Accomplishments:

- o The National Bureau of Standards (NBS)-American Ceramic Society (ACerS) five year expansion program for a ceramic phase diagram data center, was implemented. Novel procedures were developed and implemented for computer storage and retrieval of bibliographic files and for diagram digitization, computer editing, topographical manipulation, and preparation of production-quality ceramic phase diagrams.
- o A new experimental technique was developed, laser-induced vaporization mass spectrometry, for determination of time-resolved molecular-level mechanisms of very high temperature (> 4300 °C), high pressure (> 1 atm) vapor plume formation from refractory materials. The method is being applied to graphite and is yielding new mechanistic details on the vaporization kinetics needed for military applications.

- o A book on "Construction Materials for Coal Conversion--Performance and Properties Data" was completed for publication. This activity represents an evaluated compilation of data provided by the Department of Energy materials research contractor's reports. The book completes the series covering alloy and ceramic materials.
- o Using high temperature synthesis, based on the measured phase equilibria, together with x-ray crystallography, a new chemical homologous series of ternary phases has been identified in the system BaO-TiO₂-Nb₂O₅. These phases are likely to have high dielectric constants suitable for ceramic capacitors at microwave frequencies.
- o New predictive phase equilibria models were developed and applied to high-order oxide systems. The model has been validated for systems containing solids and liquids of Li₂O, Na₂O, K₂O, CaO, MgO, Al₂O₃, FeO, Fe₂O₃, Fe₃O₄ and SiO₂. Several industries involved with steel production and coal conversion (magneto-hydrodynamic, fluidized bed combustion) are planning to make use of the model for process design.

Phase Diagrams for Ceramists Data Center

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 T. Brittle, M. Lukens, P. K. Schenck, and H. Parker¹
 J. Bergen², S. Cauley², and C. Messina²

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NBS has a well-established joint data activity with the ACerS and is closely coupled with current needs, as identified by NBS and ACerS advisory committees. Recent research activity in this area has been expanded in response to the increased complexity and quantity of new phase diagrams, together with an expanded dependence by industry and others on critically evaluated diagrams and related thermodynamic data. Basic objectives are to:

- improve the literature currency of the published phase diagram volumes from 7 to 2 years;
- expand systems-coverage to include carbide, nitride, boride, compound semi-conductor and other systems, resulting in a comprehensive data base for all ceramic/inorganic phase diagrams; this expansion will more than triple the number of diagrams evaluated to date (past 50 years) over the next 5 year period;
- computerize the collection, evaluation, and dissemination procedures to the maximum extent possible; and
- enhance the utility and reliability of the phase diagrams through research developments in modeling, thermochemical optimization, computer graphics, and data base management.

(a) Evaluation/Production. Considerable progress has been made in the preparation of Phase Diagrams for Ceramists Volume VI (oxides and oxygen-containing systems) and Volume VII (halides and sulfides) for which about 6800 phase diagrams are being considered. All of the literature for

Volumes VI/VII is in the critical evaluation process and an anticipated completion date for Volume VI is December 1986. The cutoff for inclusion of literature in these volumes is January 1983 (Chemical Abstracts date). Volume VII will be the first to contain thermochemically optimized phase diagrams. These diagrams will represent computer-drawn "best-fits" to available phase diagram and thermochemical data, for alkali halide systems, and will include experimental data points for comparison along with a detailed thermochemical critique. The first series of thermochemically optimized diagrams for inclusion in the new volumes has been prepared under contract with Prof. A. Pelton of The Ecole Polytechnique, in Montreal, Canada.

(b) Date Base Development. Progress has continued both in software development and in file building for the bibliographic and graphics data files. The bibliographic file software, developed in collaboration with the NBS Office of Standard Reference Data, has been expanded and revised. The software provides not only for the preparation of fully transportable data files (all ASCII characters) of totally variable length but also for the generation of files to feed other data bases and any rapid-search data base management system. Each diagram has associated with it about 50 data elements which include not only the full bibliographic reference but also keyword information describing the diagram chemistry and experimental conditions. The software provides methods for easy updating, editing and rearranging of the data elements. It also allows the inclusion of Data Center "bookkeeping" items to keep account of file history and to provide the links to the phase diagram graphical data files. During the past year the keyboarding of bibliographic material for Volumes VI and VII has been completed.

The very efficient prototype graphics input and editing software developed earlier (FY84) for binary diagrams has been improved, documented as a users manual, and put into routine use. Over two hundred binary diagrams have been digitized and edited for inclusion in Volume VI. Similar software for ternary systems has been completed and is being tested for routine use by the Research Associates.

(c) Modeling/Optimization. Current activities focus on: (1) the development of new solution models for phase diagram optimization and prediction (2) incorporation and testing of NBS-developed solution models, and others, into existing computer codes for phase diagram optimization, (e.g.; K. Spear, Penn State), (3) application of the THERMFACT computer code, with its extended regular solution model, to phase diagram optimization for relatively simple molten salt systems, and (4) development of a thermodynamic data base for complex oxide systems, for use with the SOLGASMIX (Ericksson, Sweden) and other computer codes applicable to phase equilibria predictive modeling (W. Horton, consultant).

During the past year, a successful model has been developed for prediction of solution activities and vapor pressures in binary and higher order systems containing compounds (solid and liquid) of Li_2O , Na_2O , K_2O , CaO , MgO , Al_2O_3 , SiO_2 , FeO , Fe_2O_3 , and Fe_3O_4 . This model has a thermodynamic basis and does not rely on an assumed molecular structure of the liquid phase, or on experimental information such as mixing thermochemistry. The ability of the model to predict (as distinct from optimize) solution thermodynamic properties for real-world highly non-ideal complex oxide

mixtures is shown by the example of Figure 5. Here, the model activity data have been converted to partial pressures for comparison with our experimental Knudsen effusion mass spectrometry results.

In principle, the model should also permit calculation of phase diagrams and this aspect is under investigation. Good agreement between model and experiment has been found for the $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3$ phase diagram. One should stress, however, that the viability and reliability of this model requires continued experimental testing as additional components are added to the database. Thus this modeling effort is closely coupled with experimental determinations of solution activities and phase equilibria.

Phase Equilibria and Structural Chemistry

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Experimental research performed in support of the Data Center program, and for Other Agency projects, includes both classical determination of phase diagrams (i.e., direct phase identification) and indirect measurement based on Gibbs energy relationships. In the latter case use is made of vapor pressure measurement using unique NBS facilities. These thermochemical measurements of phase equilibria are particularly useful for testing solution models under development for phase diagram optimization and prediction. The classical phase equilibria program currently emphasizes oxide systems important to energy storage and for advanced electronic ceramics. This latter activity involves close collaboration with Industry (Trans Tech, Bell Labs) and Academia (P. Davies, University of Pennsylvania), in addition to personnel from other Groups within the Division (K. Frase, J. Ritter, J. Blendell).

(a) Stored Chemical Energy Systems. During the past year, work was performed in response to basic data needs of the Office of Naval Research (ONR) and Garrett Corporation for development of stored chemical energy propulsion systems. The system of interest is based on the exothermic reaction of a Li/Al alloy with steam to yield $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3$ phases and hydrogen, to be burned for additional thermal energy. Phase equilibria determinations have been made in the system $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3$ using structural, thermal analysis, vaporization and thermodynamic modeling techniques.

(b) Ceramic Dielectric Barium Poly titanate Systems. Various titanate ceramics are currently used for communications and defense applications at microwave frequencies varying from less than one gigahertz to four gigahertz and higher frequencies. The dielectric properties most sought after are high dielectric constant, high Q or low dielectric loss, and zero or low temperature coefficients of dielectric constant and resonance frequency. Of current interest are materials with much higher dielectric constant where the high Q is not as important but the low temperature coefficients must be maintained. Compounds with a Ba/Ti ratio of 1:4 and 2:9 are currently used and the 1:5 phase was developed as a possible candidate. Other phases with a high Ba to octahedrally coordinated ion

TEMPERATURE K

2000 1800 1600 1400 1200

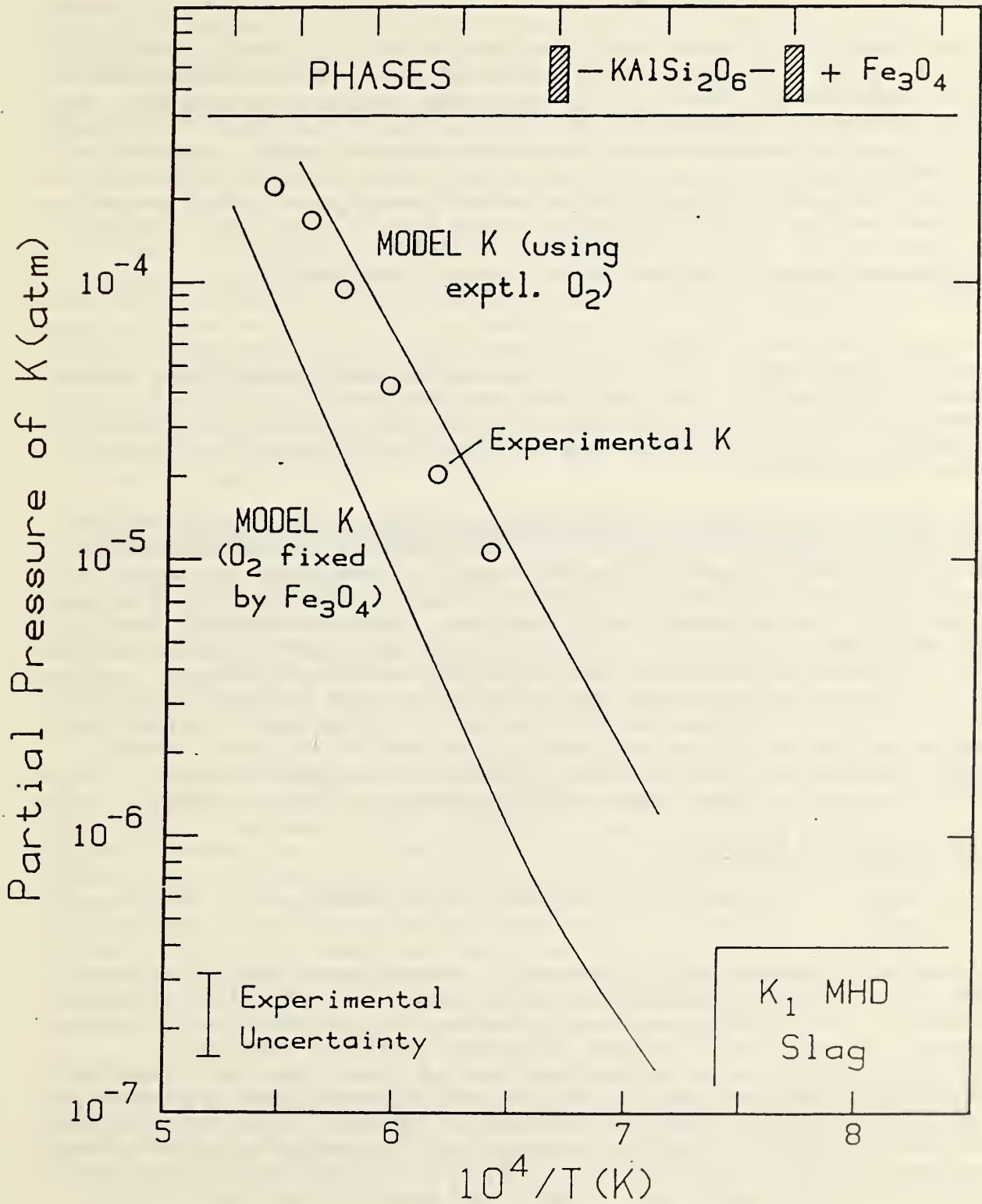


Figure 5

Model and experimental partial pressure data for K and O_2 over an MHD slag

ratio without the presence of free rutile would be expected to have such properties. Unfortunately none can be prepared in the binary system BaO-TiO₂.

Recent research has concentrated on various barium-polytitanate phases and their reactions with other oxides. Additions of low melting temperature third components include V₂O₅, MoO₃, B₂O₃, P₂O₅ and BaLiF₃. Ba₂Ti₉O₂₀, the major component in microwave filter devices, was found to be in equilibrium with Ba₃V₂O₈ and Ba₂V₂O₇ in the ternary system BaO-TiO₂-V₂O₅. However, in the ternary BaO-TiO₂-P₂O₅, rutile is in equilibrium with both Ba₃P₂O₈ and Ba₂P₂O₇, so Ba₂Ti₉O₂₀ is equilibrated only with Ba₃P₂O₈. In this system the reported phase 4BaO·3TiO₂·P₂O₅ was found to be a mixture of tribarium phosphate and two barium polytitanates. Instead of this compound there is another previously unreported ternary phase at approximately 12BaO·2TiO₂·5P₂O₅.

Because of the chemical similarity between Nb₂O₅ and TiO₂ and the valence identity between Nb⁺⁵, V⁺⁵, and P⁺⁵, we have examined in detail the ternary system BaO-TiO₂-Nb₂O₅. This very complex system contains many previously unreported ternary phases. Several of these phases may have dielectric properties of great interest in the communications industry for microwave defense applications.

(c) Neutron Diffraction of Alkali Insertion Phases. A continuing cooperative project between NBS and A.T. & T. Bell Telephone Laboratories has led to the structural refinement of a large number of new phases containing alkali ions inserted into transition metal oxides. The compound LiV₂O₅ has eluded structural refinement for a long time. This was apparently due to the use of an incorrect unit cell for indexing the pattern. Utilizing the Visser program for indexing unknown powder diffraction patterns, Dr. R.J. Cava of Bell Labs was able to arrive at a new unit cell which is more consistent with the data. This unit cell was then used to refine the neutron diffraction data using Rietveld total profile analyses. Another group of phases having the pyrochlore structure were also refined by Rietveld analysis. These include KNbWO₆, K₂NbWO₆ and KNbWO₆·0.69D₂O.

High Temperature Chemistry

J. W. Hastie, E. R. Plante, D. W. Bonnell, P. K. Schenck, A. B. Sessoms, M. Wilke

This activity develops and applies new or improved measurement techniques for the molecular-level analysis of high temperature vaporization processes. The processes occur over ceramic solids and melts, coal slags, glasses, and salts and in process atmospheres containing reducing, oxidizing, carbonated, halogenated, sulfated, hydrous, and other reactive components. These environments are characterized by extremes of temperature (typically 10 - 5000 K), gas pressure (10⁻⁶ - 10² atm), chemical reactivity, and phase complexity. The conditions and data obtained are generic to high temperature ceramic processing environments, and in applications where hot corrosion and high temperature oxidation are materials-limiting factors.

(a) Nuclear Waste Glass Processing. Industrial and DOE plans for nuclear waste storage require the waste to be incorporated into a borosilicate glass. Vapor pressure data are needed for these glass-waste forms in order

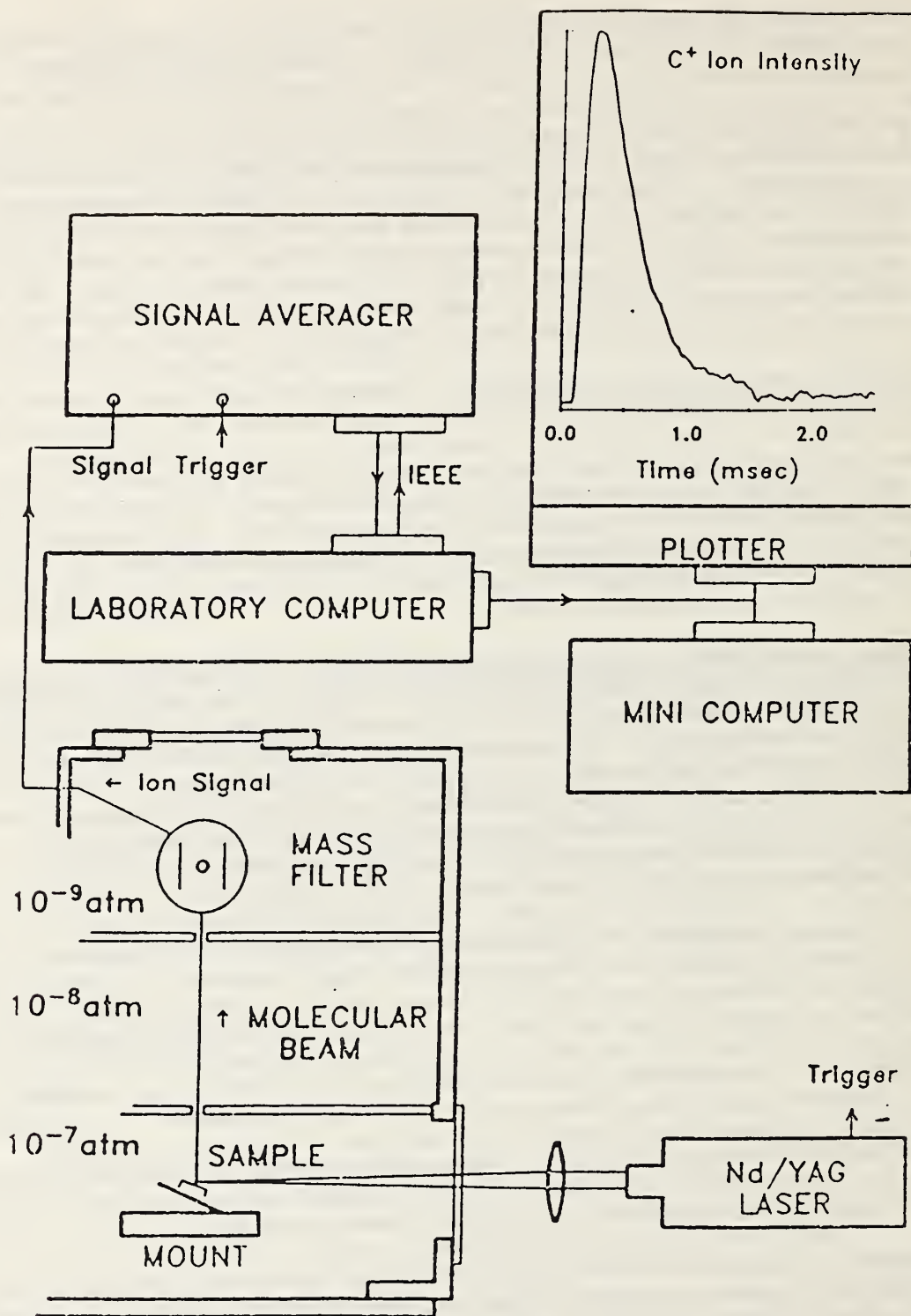
to optimize the process conditions (e.g., temperature, composition) and minimize losses of radionuclides by vapor transport during the high temperature processing of the wastes. The primary objective of the present study is to define the vaporization thermodynamics of simulated nuclear waste borosilicate glass, containing non-radioactive isotopes, as prepared by DuPont-Savannah River. Also, measurements of partial pressures for each vapor species allow activities and related partial molar thermodynamic functions to be derived. Such basic data are pertinent to the development of thermodynamic models of other nuclear waste properties such as leaching and storage durability. Special emphasis is being given to vapor species containing the following elements which in actual nuclear waste form are highly radioactive: Cs, Sr, Ru, and Re (added as a technetium simulant).

(b) Stored Chemical Energy Propulsion. Knudsen-effusion mass spectrometric measurements of species partial pressures and solution activities have been made in support of the interest in phase equilibria in the $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3$ system. The results have been used for phase diagram construction using both the classical and Gibbs energy approaches. Also, the activity data, obtained as a function of temperature and composition, will be used in developing thermodynamic models of the heterogeneous reactions involving H_2O and H_2 . An interim phase diagram has been constructed from the mass spectrometric data obtained to date.

(c) Laser-Induced Vaporization Mass Spectrometry. Degradation of materials by high powered lasers is important in, for example, the design of laser fusion processes, laser welding, laser processing of ceramics, and in the durability of refractories in defense and space applications. In addition, the use of lasers as point heat-sources has the potential for characterizing materials phase transformations at very high temperatures and under essentially containerless conditions. We have undertaken fundamental studies of laser-induced molecular level vaporization with initial emphasis on graphitic and boron nitride materials.

Figure 6 shows a schematic of the apparatus developed for these studies. A very high pumping speed is maintained in the sample chamber to simulate the environment of near-earth orbit conditions. Use of a Nd/YAG laser, with adjustable nanosecond pulse duration, and collection of mass spectral signals as a function of time provides a dynamic picture of the vaporization process. The apparatus also allows for multiple shots in a single location thereby simulating cratering and ablation processes. A technique for varying the laser beam impact angle has been developed to isolate laser/plume interaction processes. Temperature, molecular weight and other information is convoluted in the time resolved mass spectral profile and a model is under development to deconvolute these parameters.

Experiments on graphite show that this technique is capable of attaining temperatures in excess of 4200 K, that the vaporization process is approximately at equilibrium, and that measured distributions of C_n polymer species ($n=1-9$, or higher) are the expected equilibrium values.



Schematic of laser-induced vaporization mass spectrometric facility (NBS 420).

Figure 6

Knowledge of effects of high pressure and temperature on the structure, phase relations, and physical, mechanical and chemical properties of materials is necessary for their efficient industrial utilization. Such information is essential, for example, for improving our understanding of the parameters that are critical to ceramic processing and transformation toughening in order to produce more fracture-resistant ceramic products. The stability and retention of high pressure phases as toughening agents to improve the properties of materials, particularly ceramics, is a new area that requires attention. To carry out these investigations effectively, we must improve our measurement and standards capabilities at high pressures.

Representative Accomplishment:

- o The concept of obtaining transformation toughening by pressure was conceived and evaluated. The high pressure tetragonal II form of zirconia was obtained metastably, and the hardness and toughness of compacts containing this material were determined. The results confirm the concept of pressure transformation toughening. As a consequence of this, a new class of materials is now available with the potential of improving the mechanical properties of ceramics.

Pressure Transformation Toughening

S. Block, G. Piermarini, J. A. M. da Jornada¹

¹Guest Worker, Universidade Federal do Rio Grande do Sul (UFRGS) and CNPq

Two criteria are necessary for transformation toughening of a ceramic material. The first, (1), is the presence of a metastable phase uniformly dispersed in a matrix of a stable phase. The metastable phase must be denser than the stable phase or must have at least one crystallographic cell dimension less than any one of those of the stable phase. This condition produces either a molar volume increase or at least one larger cell dimension on transformation to the stable phase. The second, (2), is that the transformation must be rapid, characteristic of a diffusionless or a martensitic-type transition.

Criterion (1) above is typical for high temperature phases, and only a few examples with this anomalous behavior can be cited. However, as a general rule, denser phases are always produced in any pressure-induced phase transition. Thus, the phenomenon of transformation toughening is more general than previously thought and is not limited necessarily to zirconia and hafnia. If further major advances are to be made in this area of transformation toughening, they are more likely to be achieved by consideration of the pressure variable.

The initial problem was to retain the high pressure phase in a metastable form at room temperature upon release of pressure. Studies were undertaken varying particle size, pressure, temperature, time and the hydrostaticity

of the sample. Preliminary results indicated that all of these variables contribute to the retention of the high pressure phase, but that relatively low temperatures at elevated pressure were sufficient to make compacts containing both phases. Zircar ZYP, which is a commercially available product, was chosen as a standard zirconia powder. Compacts were made for microindentation studies to evaluate the hardness and toughness of the new materials. These studies are being carried out in collaboration with B. Lawn and B. Hockey of the Mechanical Properties Group.

Preliminary results, shown in Table 1, indicate that hardnesses for the compacts containing only the low pressure phase were only 4.4 GPa or less. Samples with some retained high pressure phase have hardnesses ranging from 9.8 to 16.9 GPa with the larger value comparing favorably with the best conventional zirconia ceramics. Moreover, the observed hardnesses appear to be a function of pressure, sintering temperature and time, with higher hardnesses being achieved through longer sintering times. A critical factor to note here is that required sintering temperatures (500 °C or less) for this high pressure process are far less than the 1100 °C temperature needed in the conventional thermal processes. The toughness of any of the samples prepared so far has not been measurable because none of the samples containing the retrieved high pressure zirconia phase (tetragonal II) has shown any significant cracks around the anvil indentation. It is these cracks which can be interpreted quantitatively in terms of toughness.

Table 1 actually has two possible variables: 1) toughening agent and 2) pressure sintering. Work is continuing to sort out these variables by completing the studies on pure zirconia and initiating similar studies on stabilized zirconia. In collaboration with L. Cook of the High Temperature Group, a search for other possible toughening agents with a lower transition pressure and with a higher usable temperature range than zirconia is being undertaken.

Pressure Phase Relations of Ceramics

S. Block, and G. Piermarini

The transformation pressure and high pressure structure of $ZrO_2:18 \text{ mol\% CeO}_2$ were studied by optical microscopy, x-ray diffraction and Raman spectroscopy with P. Miller of NSWC. Briefly, ceria doped zirconia converts to the cubic form at approximately 10 GPa. Preliminary studies were also made on yttria doped zirconia. The transition pressure and high pressure structure, i.e., tetragonal II or cubic depend on the yttria concentration. As expected, preliminary studies of hafnia indicate a similarity to zirconia.

Table 1

Micro-indentation hardness tests on retrieved high pressure samples of pure zirconia powder compacts.

SAMPLE PRESSURE	SINTERING TEMPERATURE	SINTERING TIME	SAMPLE HARDNESS	RETAINED PHASE(S)
3.5 GPa	20 °C	1/2 hr	-	LP
7.6 "	20 "	1/2 "	-	LP
3.2 "	150 "	1/2 "	-	LP
5.0 "	250 "	1/2 "	4.4 GPa	LP
8.6 "	250 "	1 1/2 "	9.8 "	LP-HP
8.5 "	500 "	1 1/2 "	13.0 "	LP-HP
8.5 "	500 "	4 "	16.9 "	LP-HP

LP = low pressure monoclinic phase

HP = high pressure tetragonal II phase

LP-HP = mixture of the high; and low pressure phases.

Kinetics of Decomposition of High Energy Materials as a Function of Pressure

G. Piermarini, S. Block, and P. Miller¹

¹Naval Surface Weapons Center, White Oak, MD

This project, which is funded by the Army Research Office, is designed to provide new information concerning the parameters that affect the kinetics of explosive detonation and thermal decomposition processes of high energy ordnance materials. The study of the phase behavior, melting point, and decomposition of HMX (a high energy ordnance currently in field use) as a function of pressure and temperature was initiated. The primary probes used in these studies are optical polarizing microscopy, fast Fourier Transform Infrared Absorption Spectroscopy and x-ray powder diffraction.

CERAMIC POWDER CHARACTERIZATION

Alan Dragoo

The formation of most ceramic materials begins with the processing and consolidation of powders. Characteristics of a starting powder, such as grain size (primary particle size), agglomerate size (secondary particle size), residual stress, internal porosity, particle shape, and chemical and phase composition influence the properties of densified ceramics attained at the outcome of the forming and sintering processes. The application of ceramic materials in advanced heat engines, as components for electronic devices, for improved cutting tools and in dense thin-layer components place critical demands on the preparation and characterization of starting powders.

The task of the Ceramic Powder Characterization Group is to improve the measurement of powder and fine particle characteristics and to advance the understanding of how those characteristics influence properties of densified ceramics. The work of the group is directed largely to the development of new Standard Reference Materials (SRM) for powder characterization, including x-ray powder diffraction, and to the improvement of measurement methodologies. Work in progress includes assessment of measurement variables in particle size measurement by x-ray sedimentation and photon correlation spectrometry, identification and interpretation of particle characteristics, correlation of powder characteristics with properties of resultant green-state ceramics, and development of SRMs to enhance the accuracy of x-ray powder diffraction. Shape analyses are being conducted on alumina wear particles, mineral particulates, and a variety of commercially derived powders to investigate relationships between shape parameters and powder generation processes.

The work of the group is carried out primarily in two facilities: the Automated X-ray Diffraction Laboratory and the Fine Powder Laboratory. In addition a scanning electron microscope is used routinely for direct characterization of powders. During this fiscal year a new semi-automated x-ray powder diffraction system was selected and purchased. This system is scheduled for delivery in July 1985. The system has much higher resolution and sensitivity than x-ray diffraction equipment currently in use at NBS. When it is fully automated, the system will permit the rapid acquisition of high-quality phase data, both at room temperature and at temperatures to 1600 °C in vacuum. The high-temperature capability will permit the measurement of thermal expansion and the study of phase changes. In addition to phase identification studies, the system will be used to obtain data on sample texture, residual stresses and crystallite size.

Both formal and informal scientific collaborations extend the range and variety of the research activities. Under a program established with the Joint Committee for X-ray Powder Diffraction-International Centre for Diffraction Data (JCPDS-ICDD), research associates, with technical guidance

by NBS, provide critical evaluation of published powder diffraction data, develop a numerical data base and provide "standard" powder patterns on selected materials. Collaborative work in x-ray powder diffraction also is carried out with groups at Alfred University and the University of Maryland. Industrial, academic and governmental laboratories provide a variety of ceramic precursor powders for the NBS research program. Beginning this year work will be undertaken to provide samples, measurement procedures, data and data analysis as part of an international round-robin in characterization of starting powders for ceramic materials for use in advanced heat engines.

Representative Accomplishments

- The second set of samples of SRM640a, Si x-ray line standard, were verified with respect to purity and consistency of the lattice parameter.
- Alumina powders were spray-dried to form agglomerated spherical particles which were subsequently calcined to yield either soft or hard agglomerates. The agglomerates will be incorporated into samples for Nondestructive evaluation (NDE) studies of processing flaws.
- Iron-rich centers were identified in pits which developed in the cristobalite (SiO_2) layer which formed on silicon carbide under active oxidation conditions. The iron was present as an impurity in the silicon carbide ceramic and is believed to have segregated due to the low oxygen activity at the SiC-SiO₂ boundary.
- Temperature and oxygen partial pressure conditions were established for the nondestructive incorporation of silicon carbide whiskers into a yttria-stabilized zirconia/zircon matrix.

X-Ray Powder Diffraction

C. Hubbard, C. Robbins, A. Dragoo, H. McMurdie*, W. Wong-Ng*, M. Morris*, E. Evans*, M. Mrose*, B. Paretzkin*

*JCPD-ICDD Research Associates

Improvements in the resolution and sensitivity of x-ray diffractometers and in computer control and data processing for those instruments have expanded the already wide application of x-ray diffraction in research and industry. This expanded use of x-ray diffraction has increased the need for standards, for accurate powder diffraction data, and for improved measurement procedures. Automated search procedures for rapid phase identification have underscored the need for a reliable data base of x-ray powder diffraction data.

Quantitative x-ray powder diffraction (QXRD) is of major importance to many industries, including electronic and structural ceramics. QXRD is often the only method available for determination of the concentration of phases in

materials. Unfortunately, QXRD methods are traditionally time consuming and inaccurate due to the absence of standard procedures. Those limitations have hindered the ability of industry to characterize fully solid phase materials.

Development of SRMs and improvement of procedures for x-ray powder diffraction are objectives of the Ceramic Powder Characterization Group. Several XRD SRM studies are currently in progress, including: selection of a new Si powder for use as a line position standard; selection of three materials for use as x-ray intensity standards; selection of materials for a XRD profile standard; establishment of a cristobalite standard for quantitative XRD; and refinement of a large d-spacing standard.

The Powder Diffraction File (PDF) is of major importance to the mining, ceramics, metals, and other materials industries where XRD is used to identify solid phases. NBS assures that measurement methods and essential reference data are available through its own research and by collaborating with the JCPDS-ICDD to improve the internationally used PDF.

The primary objective of the ICDD-NBS program is to produce very accurate x-ray powder diffraction patterns. An automated diffractometer is used for digital data collection. The data are processed with an extensive software system. Accuracy in 2θ measurements are typically $\pm 0.005^\circ$ compared with $+0.02^\circ$ for strip chart recording procedures used on nonautomated instruments. Intensities of the reference patterns are accurately recorded.

While reference patterns from the collaborative ICDD-NBS program are of high accuracy, the majority of patterns in the reference file are not. Work has proceeded this year on identifying and evaluating older powder patterns for common phases. New powder patterns are being prepared for materials where inaccuracies in line positions, missing diffraction lines and errors in data file are found to exist. In addition to experimentally measured patterns, a program is proceeding to supplement the data file with additional numbers of calculated patterns. To improve the dissemination of the extensive PDF and to increase the rate of data retrieval, optical disc systems are being investigated for storage of the data base.

Powder Characterization

A. Dragoo, C. Robbins, D. Minor

A determination of a particle characteristic, such as size, shape and porosity, generally employs the measurement of a macroscopic property which is often related in an indirect manner to the microscopic characteristics of many particles. The science of powder characterization involves fundamental physics of the measurement process, sample preparation procedures which present problems in interfacial and colloidal chemistry, and the interpretation and comparison of observations which are confounded by different statistical assumptions and distributions. Thus, it is not sufficient to provide, for example, an SRM for calibration of various particle size measuring apparatus without assuring that the procedures and data interpretation of those different instruments yield results that can be

compared. In the case of starting powders for ceramic processing, the major significance for powder characteristics lies in their impact on properties of green-state and sintered ceramics.

Currently experimental procedures and data analysis are being examined for the x-ray sedigraph, photon correlation spectrometer and microscopy/image analysis. In the near future Brunauer-Emmett-Teller (BET) procedures and mercury porosimetry also will be examined. Fine silicon nitride and alumina powders, and where appropriate, standard latex or polystyrene spheres, are being used for size measurements.

Measurement methods for particle shape analysis are being applied to powders from a variety of sources to develop meaningful numeric descriptors for particle shape. Data presented in Figure 7 were obtained from alumina wear particles. The data are presented in a three-dimensional plot which shows the distribution of a number of particles (vertical axis) with respect to DMAX (the maximum diameter or chord) along the horizontal axis and a form factor, Form PE, along the receding axis. Form PE equals 1 for a circular projected area and is less than 1 for an ellipse or an irregular shape. The plot shows, first, that most of the measured particles had a DMAX $< 1 \mu\text{m}$ and that the smallest particles had approximately circular projected areas. Secondly, the plot shows that the projected areas of the large particles became increasingly irregular as the particle size increased.

Preparation of Green State Ceramics for Nondestructive Evaluation

C. Robbins, W. Coblenz¹

¹Formerly of the Structural Science Group, now at Norton Co.

The objective of this task is to prepare "green" (unfired) ceramic compacts with known flaws for exploratory studies by nondestructive methods as well as by established destructive methods. Characteristics of the starting powders and processing conditions that are used prior to the sintering of ceramics are sources of many limiting defects that lead to early failure of finished components.

During this fiscal year work was initiated on a high-purity alumina powder. The powder was characterized by a variety of measurement techniques, and a large quantity of powder was processed to produce green compacts. The compacts are to be studied at NBS by a variety of NDE methods, including ultrasonics, thermal wave and small angle neutron scattering (SANS) methods. SANS and ultrasonic measurements have been completed on an initial group of alumina samples prepared without binder and other organic additives.

Structural Ceramics

A. Dragoo, D. Minor

Silicon carbide and silicon nitride ceramics generally contain a variety of second phases. Those phases may be introduced intentionally - for example, as sintering aids, reinforcing fibers or a pore filling phase such as free

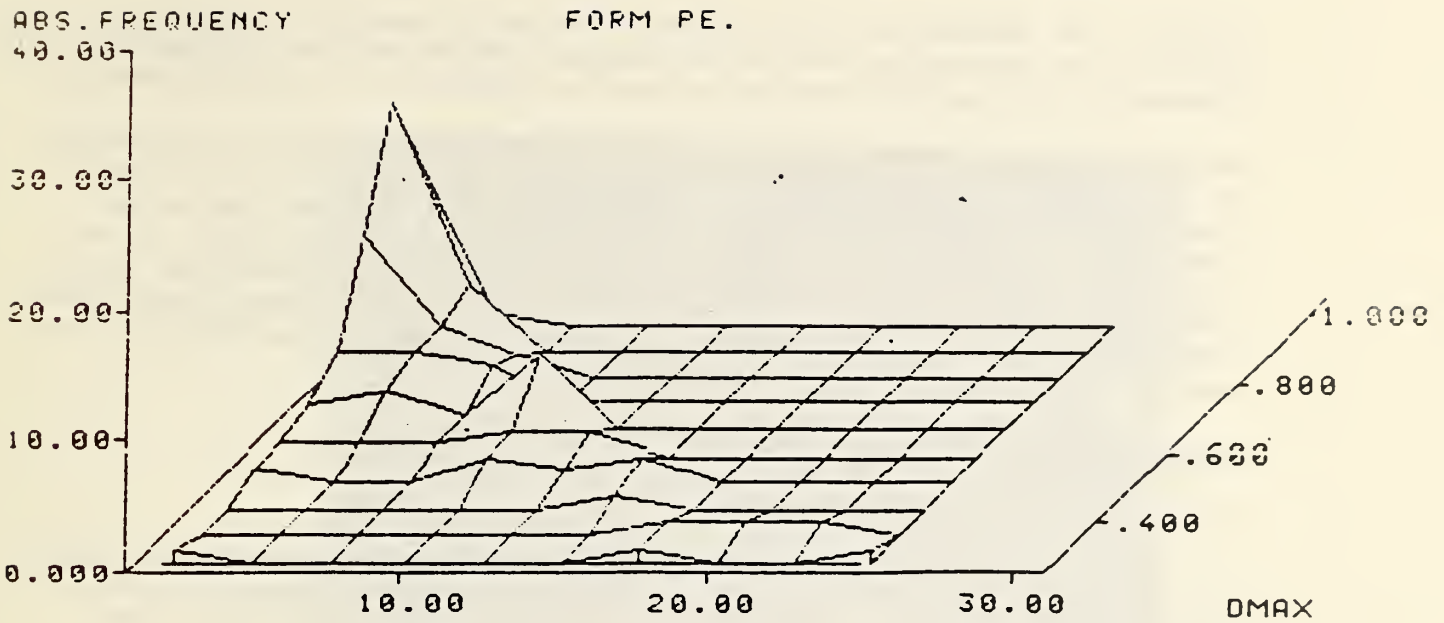


Figure 7. Size and shape analysis of alumina wear particles. The plot shows the distribution of number of particles with respect to particle size (D_{MAX}) and projected particle shape (Form PE): Form PE = 1, circle; <1, ellipse or irregular shape.

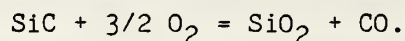
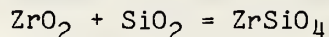
silicon - or inadvertently as impurities during processing. Milling of precursor powders often introduces tungsten carbide and iron inclusions. The presence of the second phase may affect the reactivity of ceramic material.

Studies of a SiC ceramic containing iron as an impurity showed the presence of iron-rich regions in pits in an oxide layer (cristobalite) which was formed on a SiC substrate under active oxidation conditions (low oxygen pressure). A scanning electron micrograph with superimposed trace of the iron x-ray signal is shown in Figure 8. At higher oxygen pressures (air at 1400°C) oxidation of the SiC substrate is passivated by a dense oxide layer. Under those conditions hematite nodules were observed to have formed on the surface of the oxide layer.

Zirconia-Silicon Carbide Composites

D. Minor

The incorporation of SiC whiskers into an oxide matrix requires both control of the chemical reaction during processing so that the whiskers are not destroyed and an approximate matching of the thermal expansions of the whiskers and the matrix. Since the thermal expansion of SiC is closer to that of zircon, $ZrSiO_4$, than to that of zirconia, ZrO_2 , incorporation of SiC whiskers into the zirconia matrix requires the generation of a zircon sheath around the whiskers without completely degrading the whiskers. The thrust of the present work has been to elucidate the temperature - oxygen partial pressure, $P(O_2)$, relationship between the competing reactions



Pressed compacts of various compositions were heated in a controlled atmosphere furnace, the resulting material was analyzed by x-ray diffraction and fracture surfaces were examined with a scanning electron microscope (SEM). Figure 9 shows a micrograph of a fracture surface. Preliminary evidence shows that the whisker distribution and not the pressing regimen has the greatest direct effect on the coherency of the final fired product. Under the appropriate $P(O_2)$, the SiC whiskers showed little or no degradation and negligible bonding to the matrix.

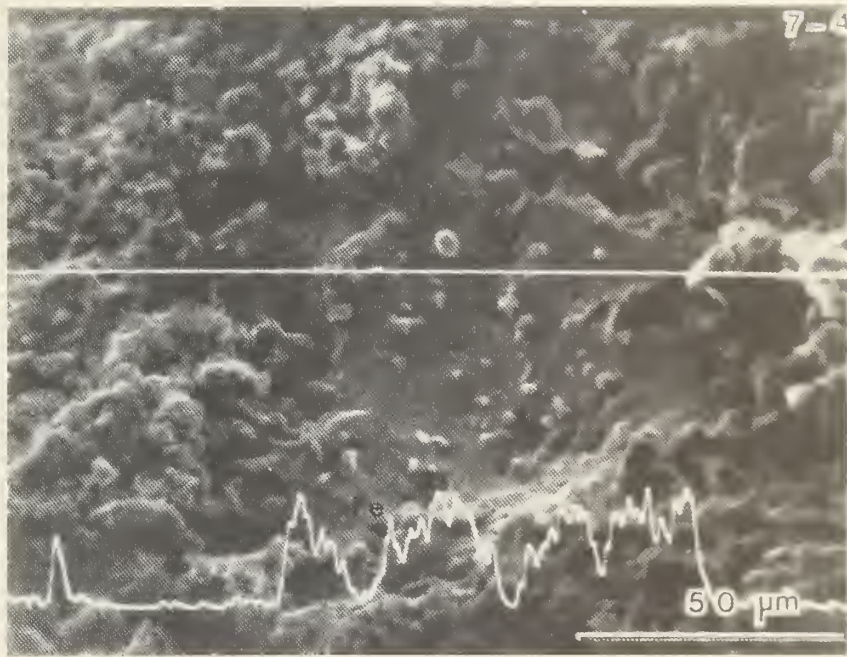


Figure 8. Scanning electron micrograph of cristobalite (SiO_2) layer on a SiC substrate with a pit containing a high concentration of iron. The superimposed line at the bottom of the figure is the iron x-ray signal.

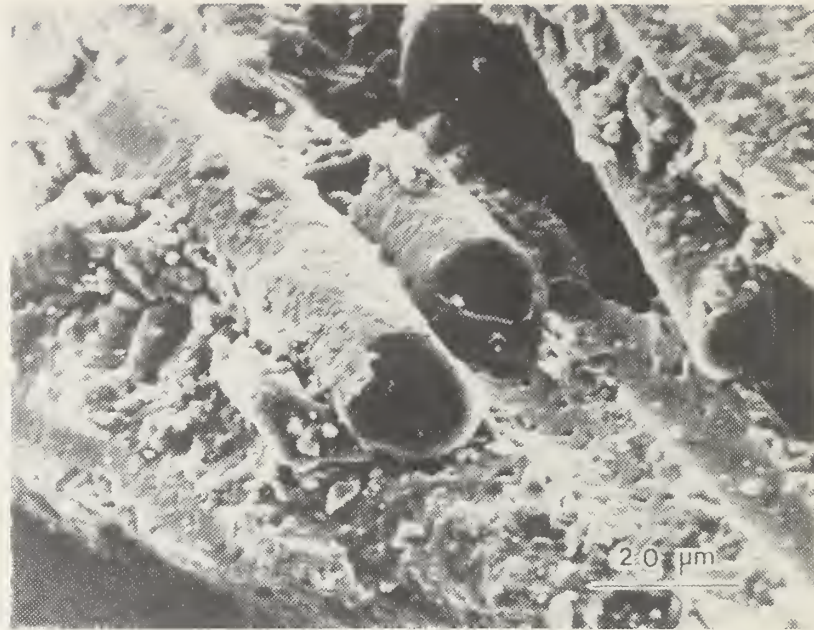


Figure 9. Scanning electron micrograph of a fracture surface from a SiC whisker/zirconia matrix composite.

The objectives of this Group are to provide essential data, accurate measurement methods, and a quantitative mechanistic understanding of chemically- and biologically-mediated events that control the design, processing, and the performance or durability of novel or improved inorganic materials. Consonant with recent programmatic restructuring of the Ceramics Division and the Institute for Materials Science and Engineering major new Group task thrusts feature strong concerted links with major NBS initiatives, including advanced ceramics and biotechnology.

Special emphasis has continued on generating basic understanding of the impacts of latest materials developments on service environments and concurrently quantitating those environmental factors that dictate durability of both end-use inorganic materials and their processing components. Thus, Group research has provided information on prospective means for selective bioextraction, recycling, and preservation of strategic and precious materials, especially metals, in inert ceramic containments.

Within this framework, a novel molecule-specific surface imaging capability under continuing development and demonstration, has already accelerated our in-service performance testing of innovative specialty designed organometallic coatings. These novel materials represent multi-billion dollar Federal investments in defense and postal services. Our imaging capability also presages unique on-line process monitoring for, and durable reactor developments crucial to, emerging national concerns for strategic and precious metals bioextraction and bioprocessing.

Representative Accomplishments:

- o At the request of the U.S. Navy, the first world-wide interlaboratory comparison of methods for the trace quantitation and chemical speciation of a major organotin biocide, tri-n-butyltin cation, has been concluded. The methods study supports implementation of organotin-containing antifouling paint coatings providing 100% antifouling performance at sea for five to seven years, with initial fuel cost savings for the U.S. estimated to exceed several hundred million dollars annually.

- o The solution and solid state chemistry of a water-stable metalloorganic complex of terbium(III) has been measured with respect to its efficacy and durability in a broad spectrum of organic coatings applied to postage stamp papers in automated processing. The new taggant's compatibility and performance exceeds that of other phosphors. Optical data (excitation and emission wavelengths, quantum efficiency) owing to careful molecular design show major new cost savings. Homogeneous, stable solutions have been synthesized in bulk and delivered in a non-toxic, non-flammable medium on a scale suitable for forthcoming multi-million stamp production. A process patent application has been submitted.

- o Major components of a molecular surface imaging and bulk materials characterization facility have been demonstrated, including Fourier transform infrared (FTIR) spectroscopy to characterize coal beneficiation by microorganisms, microscopic imaging to elucidate metal accumulation on living microorganism with fluorescent metal dyes and epifluorescence microscopy, and solid state NMR used to develop novel structure/property relationships and characterize non-destructively the structure of both crystalline and amorphous polymeric organometallic solids.
- o A bioprocessing facility has been assembled consisting of a high pressure-temperature bioreactor and percolation columns, to be coupled to an epifluorescence microscope and FT-IR system for non-destructive on stream bioprocess monitoring. The system supports new studies on potential novel, cost-effective methods for strategic metal bioleaching and recovery, coal beneficiation and iron ore beneficiation, all designed to provide quantitative understanding, data, and process optimization for biotechnological processing systems.

Inorganic Materials Bioprocessing

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¹Guest Worker, University of Siena

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⁵Guest Worker, University of Cincinnati

Strategic minerals are critical to our economy and national defense. Yet we rely on other countries for a number of raw materials, for which we lack cost-effective technology to mine available domestic low-grade deposits or recover critical elements from process or waste streams. Microorganisms that solubilize or precipitate inorganic materials offer low cost alternatives to conventional processing and beneficiation of ores and fossil fuels. This is especially evident in the metal producing and processing industry now faced with leaner domestic ores, strict environmental regulations and increasing energy costs. Accordingly, bacterially-assisted hydrometallurgical leaching of low grade copper ores in the western U.S., for example, accounts for >200,000 tons of copper production annually (nearly 20% of the U.S. total) and is a major reason for the survival of the domestic copper industry in the current depressed world market. However, this biotechnology is still applied in a primitive fashion because we lack scientific understanding of fundamental solubilization mechanisms and rate-limiting or -accelerating factors. Moreover, progress in this area has been seriously hindered by measurement obstacles, especially in characterizing surface chemistries of substrates in intimate contact with adsorbed microorganisms.

During the past year we have begun studies to explore strategic metals biorecovery and microbial beneficiation of coal by sulfur and metal removal; and domestic iron ore upgrading by phosphorus (P), sulfur (S), silicon (Si) removal. Our research applies novel ultratrace molecular

speciation methods to surfaces and solutions associated with microbial reactions in order to understand fundamental mechanisms, reaction products and intermediates and optimization of processing conditions (Figure 8). In this area we have applied our Group's experience in biocorrosion of finished metals to the study of microbial dissolution of metal ores and minerals, and provided the conceptual framework for selection and design of desirable bioreactor containment materials featuring resistant ceramics.

We have conducted a critical literature review, compiling the status and potential of microbial processing for precombustion removal of sulfur, metals and other undesirable elements from coal, and for biological liquefaction or oxygen/nitrogen removal from coal. Concurrent laboratory experiments evaluated some promising candidate organisms that degrade model compounds with structural similarities to coal. For example, a strain of Streptomyces decarboxylates vanillic acid, and when incubated with coal, appears to remove oxygen as CO_2 , as shown directly by diffuse reflectance FT-IR of the active process coal substrate.

High grade steels require removal of phosphorus impurities, and this is most effectively done at the raw materials (ore) stage. U.S. ores are high in P and S and Si impurities, and the cost of their removal is high. Microorganisms are reportedly capable of solubilizing certain forms of these elements and potentially offer low energy, low cost alternatives to current technologies. However, nothing is known about solubilization of these elements from ores by microorganisms. Our work has shown production of volatile P metabolites by iron corroding, anaerobic bacteria. We are now studying iron ore from a Michigan mine for P, S, and Si removal by aerobic and anaerobic bacteria.

A teflon lined high pressure/temperature bioreactor system with gas and liquid sampling ports has been assembled for on stream bioprocess monitoring by epifluorescence microscopy, FT-IR, and other molecular speciation instrumentation. Of special interest is the investigation of the resistance of ceramic materials to corrosive biogenic metabolites at elevated process temperatures and pressures. While conventional container materials such as stainless steels are highly susceptible to these agents, relatively inert ceramic containment offers prospects for fully exploiting the developing biotechnology.

Initial work on processing has concentrated on fluorescent metal dye systems to visualize metal species on active bacterial cells and in solution. Quantitative epifluorescence microscopy showed that tin bioaccumulation on cells is measurable with the fluorescent ligand 3-hydroxyflavone. Experiments underway using porous glass beads with tin coordinated to mercapto groups covalently bonded to the glass also show that tin(IV) can be imaged nondestructively on a materials surface with the flavone. These experiments also reveal metal bonding characteristics on cells and materials.

Initial metal leaching experiments have examined the effects of cinnabar (HgS) on microbial metal sulfide solubilization, since this mineral is considered a potential toxicant when present in an ore supply. Previously, we demonstrated that a mercury-resistant strain of the commercial ore-solubilizing bacterium Thiobacillus ferrooxidans had the

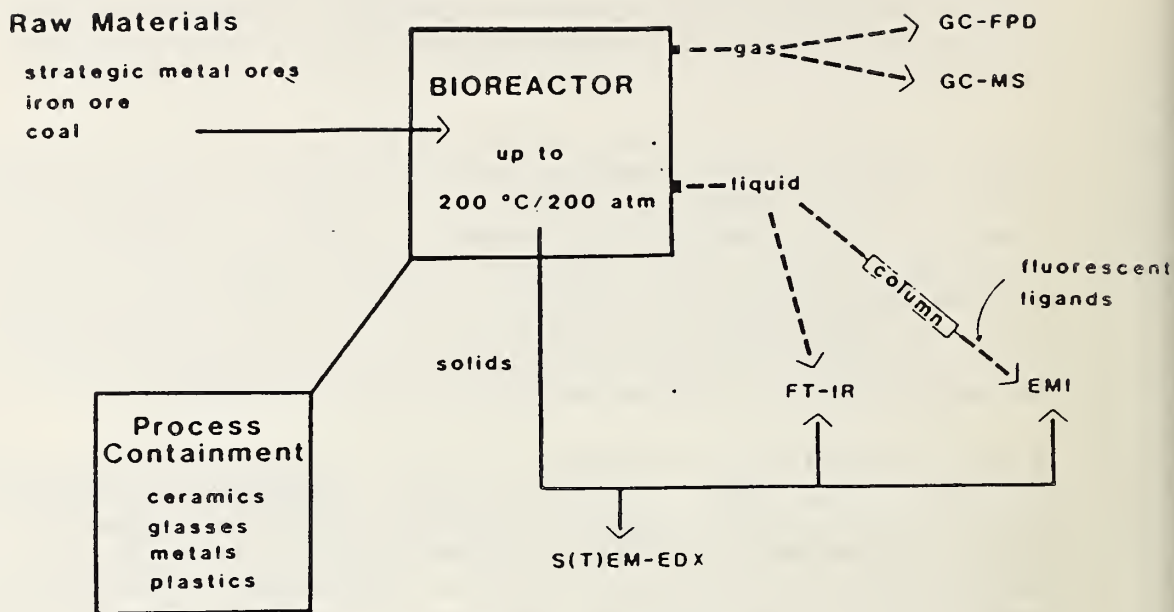


FIGURE 8. Components and flow diagram of the new bioprocessing facility. Raw materials are processed in a teflon-line bioreactor by micro-organisms, or their exocellular metabolities, at ambient conditions or under elevated temperatures and pressures. On-stream analyses (dashed lines) of gases is performed by gas chromatography (GC) coupled to an element-specific flame photometric detector (FPD) or mass spectrometer (MS), and of liquid samples by Fourier transform infrared spectrophotometer (FTIR) or epifluorescence microscopic imaging (EMI), following liquid chromatographic separation with post-column derivatization by metal-specific fluorescent ligands to detect and quantify key process products. Solids are also characterized off-line (solid lines) by surface imaging methods, including scanning/transmission electron microscopy with energy-dispersive x-ray microanalysis (STEM-EDX), and the mentioned FTIR and EMI techniques. Process containment is critical under such highly corrosive bioprocessing conditions and evaluations of the durability of various conventional and advanced non-metallic contact materials are being performed to insure appropriate development of cost-effective scale-up bioprocessor developments.

potential to process ores in the presence of mercury. In collaboration with F. Baldi of the University of Siena, we are examining mercury-resistant T. ferrooxidans from cinnabar deposits in Italy. The organism has oxidized pyrite the presence of HgS, producing Hg⁰. A Hg-sensitive strain was inhibited under the same conditions. Thus, mercury-resistant bacterial species may be useful in bioprocessing of cinnabar-containing ores.

Inorganic Materials In-service Performance and Durability Studies

E. J. Parks, W. R. Blair, F. E. Brinckman, T. L. Lockhart¹, C Matthias², J. M. Bellama², D. Ollivon³, C. Valeiras-Price², P. Dougherty²

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Non-Destructive Nuclear Magnetic Research (NMR) Measurement Methodologies for Ceramic Materials Analysis. The past year has seen important new developments in our basic research effort to develop new measurement methodologies and technical data bases for the characterization and prediction of materials properties using NMR spectroscopy. This project has led to the discovery of highly accurate NMR/structure correlations from solid-state NMR measurements of structurally-characterized organotin(IV) substrates and represents the first time that this fundamental capability of solid-state NMR has been recognized explicitly and exploited. With this new data base, we are now able to carry out the molecular characterization of organotin(IV) materials with a high degree of refinement. Most importantly, our approach is general and has clear implications for numerous other spin-active metals or metalloids which play critical roles in inorganic and organometallic materials, including ceramics, glasses, and catalysts. The accuracy of the new relationships (of C-Sn-C angle to the magnitude of tin-carbon J coupling, [¹J]) has been demonstrated. Several predictions of the molecular structure were shown to be correct by subsequent x-ray structure determination carried out by several groups of university collaborators. We have established the ability of the technique to distinguish between different, closely-related crystalline modifications of a single compound and to indicate the presence of more than one molecular structure within a single modification. Preliminary results suggest that this may become the most sensitive and convenient method for revealing polymorphism for a range of inorganic materials. With this NMR technique we have identified an error in a published single-crystal x-ray structure.

Obvious applications of interest to ceramics science are the capabilities of the new methodology and technical data base for use in the determination of molecular structures of both amorphous and polymeric precursor inorganic materials. We have carried out detailed structural analyses on a number of organometallic polymers.

Innovative Coating Technologies-Materials Design, Synthesis and Performance Testing. Two major categories of large-volume commercial specialty coatings are now emerging, particularly as stimulated by innovative coating requirements. In one category are phosphorescent taggants commensurate with existing automated

facel-cancelling equipment, applied to 40 billion pieces of mail per year. In the second category are slow-release biocidal antifouling coatings used to protect ships, buoys, and wooden pilings from marine microorganisms.

State-of-the-art tagged coatings have given serious problems because they consist of an organic varnish charged with a high percentage (10-20 percent) of immiscible inorganic phosphor (typically zinc orthosilicate doped with manganese). Such coatings are readily abraded at the expense of phosphor brightness. Corrective measures are necessary that cost well over twelve million dollars annually, since false negative stamps must be examined and cancelled manually, causing substantial added labor costs and delays. Available metalloorganic phosphors have a drawback in low quantum efficiency (brightness). We have developed a metallorganic terbium complex in which eight molecules of a bidentate heterocyclic aromatic compound [2,6-pyridine dicarboxylic acid (DPA), or its sodium salt], are bonded to the central terbium in a single aquated macromolecule. Although a pure tris-DPA solid metallorganic complex synthesized from the same components had been known for years, our study of the complex in aquatic solution proved distinctly different properties (Figure 9) detected only by microbore chromatography coupled with epifluorescence microscopic imaging (EMI). We have demonstrated that eight ligand groups, surrounding the Tb ion in solution, contribute additively to the maximum phosphorescence. In the crystalline phosphor, only three DPA molecules are accommodated by the central Tb(III) atom. The high quantum efficiency resulting from extended ligand interactions is retained on mixing the aqueous solution into the organic varnishes in current production. The next result is an end-process phosphorescent coating in which trace quantities of terbium (0.03 to 0.11 percent) as the miscible metalloorganic complex perform more effectively than 10-20 percent of current inorganic phosphor in domestic use.

This novel phosphor, moreover, holds the promise of direct application of an aqueous solution rather than a varnish to certain papers, which would greatly enhance the clarity and the esthetic value of numismatic stamps. We expect to apply FTIR to the detailed characterization of two predicted bonding situations affecting a single molecule: outer sphere coordination of terbium with the carboxylic acid substituents of DPA, and inner sphere coordination between nitrogen and terbium.

Coatings in the second category, organotin containing antifouling materials, will experience increasing usage during the next few years, affording five to seven years of antifouling protection for each application and saving hundreds of millions of dollars annually in fleet fuel costs. We have developed molecular speciation methodology to allow assessment of the environmental impact of the new organotin antifouling formulations. Of critical importance to any monitoring program for new materials with environmental applications are standard methods and reliable reference materials for assurance of data quality, reliability, and intercomparability of data. We have completed an international intercomparison of organotin measurement methods. Thirty-five participating industrial, government, and academic laboratories reported results of the analysis of our chromatographically-prepared aqueous tributyltin research material (Figure 10).

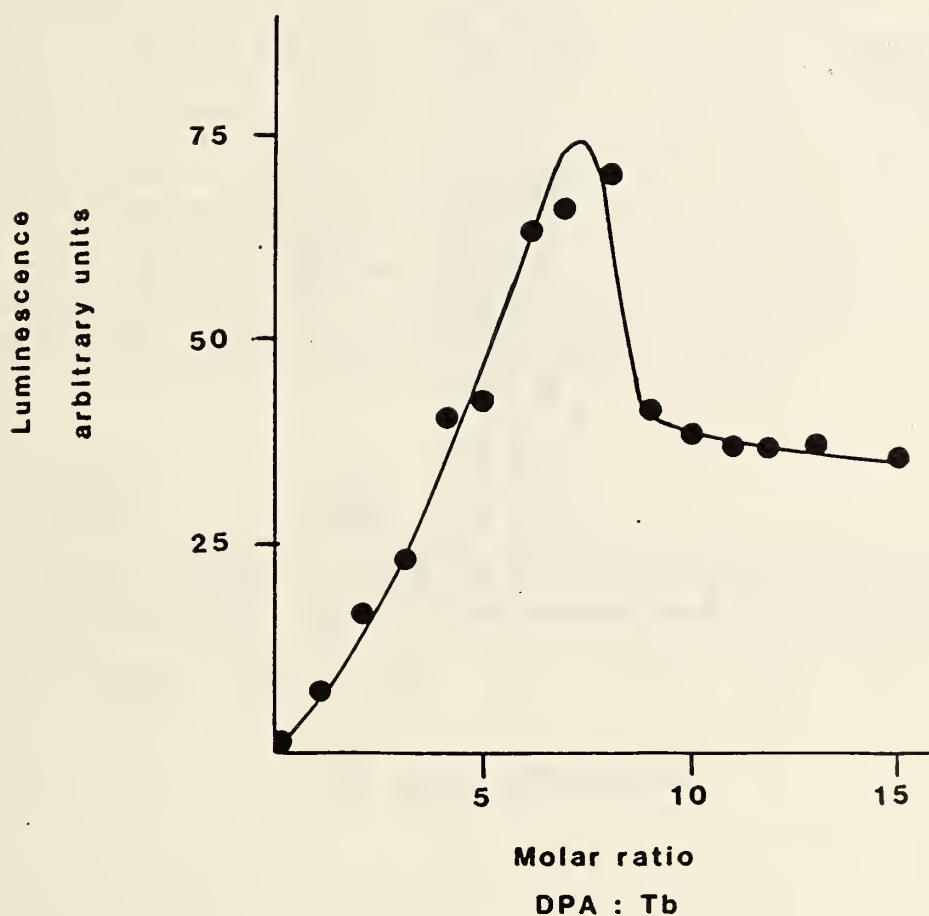


FIGURE 9. A new measurement concept is providing breakthroughs for design of novel phosphor coated materials. The Group-developed μ -bore HPLC coupled with an on line epifluorescence microscope imager (EMI) as detector has permitted us to demonstrate the optimal stoichiometry versus luminescence in aqueous terbium(III) DPA complexes, a previously unknown phenomenon. Further applications of μ -HPLC-EMI have allowed effective synthesis and incorporation of the new phosphors in major-scale postage stamp testing, where its demonstrated durability and quantum efficiency presages significant cost savings of \$12-25M per year.

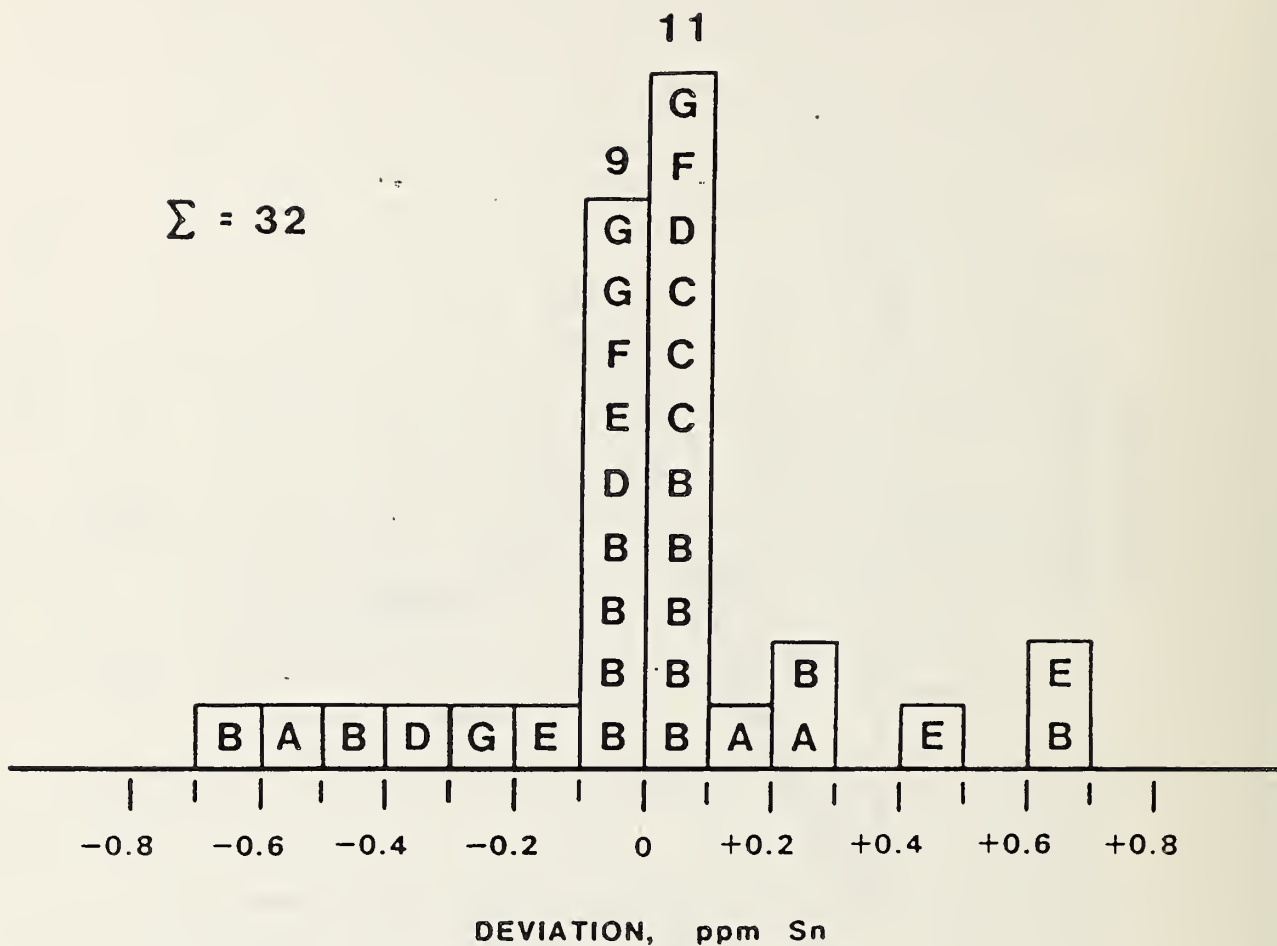


Figure 10. The frequency distribution of reporting laboratories in six countries (total = 35, 3 outliers not shown) correlates errors in total tin analysis methods (A through G) at their option. The true value of Sn in the tri-n-butyltin moiety determined at NBS by three independent methods (NAA, GFAA, GC-FPD) was 1 ppm nominally in the aqueous reference solution supplied. No single method was statistically favorable in the present study, but more than half (57%) of the participating laboratories reported results within RSD = $\pm 10\%$.

The new organotin coatings technology carries with it potential adverse environmental impacts from the leached biocide. We have developed monitoring methodology to investigate the environmental fate and effect of butyltin compounds, including biodegradation, bioaccumulation and partitioning. Hitherto, investigations in these areas were limited by the lack of reliable butyltin chemical speciation measurement methods in seawater at parts-per-trillion (environmental) levels.

Our new measurement methods also support studies characterizing rates and mechanisms of tributyltin degradation in estuarine environments. We find that biodegradation of tributyltin at ppb levels in Chesapeake Bay samples is slow unless nutrients are added to encourage microbial activity. This results in apparent debutylation to less toxic di- and monobutyltin species. However, analyses of surface microlayers and biofilms on or near tributyltin painted ship hulls revealed the presence of tetrabutyltin, which we reported for the first time in the environment, and other tin-containing metabolites. This suggests a more complex chemical pathway in the environment than heretofore believed, including redistribution reactions. This has important implications for the impacts of tributyltin use, since biofilms are present between the antifoulant paint and the surrounding seawater. Our nondestructive surface analysis facility, including FTIR and epifluorescence microscopy components, are now being applied to examine these surface reaction mechanisms.

PROCESSING

The Structural Science Group is a newly formed group whose focus is the study of the structure of ceramic materials and the relation of this structure to the processes that formed it (ceramic processing) and to the properties and performance that it determines. Characteristic structural features of ceramic materials range from the molecular, or nanostructure scale to the microstructural level. Important features at the molecular level include crystalline defects (vacancies, interstitials, dislocations, etc.); interfaces and grain boundaries; and impurity chemical concentrations. At the microstructural level important features include grain size and morphology; second-phase inclusions and pores; and distributions of these entities.

Ceramic structure lies at the heart of surmounting the two major impediments to the production and use of advanced ceramic materials. The first of these impediments is the ability to capitalize effectively on the unique properties that advanced ceramics have ("use what we have"). The uninitiated designer is not familiar with these properties, and the key materials data and understanding required to educate him are lacking. The second impediment is that understanding of advanced ceramic materials is not "mature" enough to tailor properties to a specific application ("develop what we need"). The experienced ceramics designer would like to specify the property combination needed for a specific applications, but frequently cannot due to a lack of understanding of how the properties can be achieved by ceramic processing. Knowledge of structure addresses both of these areas. Structure controls the properties of the ceramic materials and is determined by the ceramic processing. Understanding of these connections can lead to effective ceramic design.

The research effort has two main areas: Fundamentals of Interfaces, and Structure/Property Relations. In the first area, interfacial properties, such as interatomic forces, surface and grain boundary energies, defect concentrations and formation energies, and impurity species are studied and related both to ceramic sintering and to brittle fracture. In the second area, the relations between microstructural features and fracture behavior are studied (toughening mechanisms at low temperature and creep rupture mechanisms at elevated temperature).

Representative Accomplishments

- o The observation that otherwise stable interfaces (grain boundaries and thin liquid films between grains) can be induced to migrate by the diffusion of a solute into the solid has led to new understanding of the driving force for interfacial migration.
- o Growth of quartz seed crystals in a sol gel environment has been observed. This is an initiated step in the low temperature production of tough transparent ceramics for high performance applications.

Diffusion Induced Boundary Migration in Ceramics

J. E. Blendell and C. A. Handwerker¹

¹Metallurgy Division, IMSE

Interface migration due to diffusion (DIGM) that occurs at low temperatures leads to alloying at much faster rates than predicted for diffusion with static interfaces. Liquid film migration has been observed for the first time in a ceramic system. Fine MgO powders were mixed with V₂O₅ and heated above the melting point of V₂O₅. The MgO grains coarsened and spheridized. Upon addition of NiO (or CoO) the liquid film between the MgO grains migrated against its radius of curvature and formed a solid solution in the region swept out. This is in agreement with a model based on the coherency stress as the driving force for this previously unexpected boundary migration. While this type of boundary migration has been observed in a wide range of metallic systems, the conditions for migration in ceramics were not known. Experiments to observe boundary migration in the absence of a liquid film are currently under way.

Closure and Repropagation of Healed Cracks in Silicate Glass

E. R. Fuller, T. A. Michalske¹ and E. R. Fuller

¹Sandia National Laboratories

Crack closure and subsequent repropagation of healed cracks were studied in soda-lime-silica and vitreous silica glass. Cracks were observed, by birefringence pattern of the crack-tip strain field, to close against a finite load at humidities between 0.01 and 100 percent. The force associated with crack closure (0.15 J/m²) was predicted by a model that involves hydrogen-bonded linkages of surface adsorbed water molecules. The fracture energy to reopen healed cracks in vitreous silica has been determined to be in the range of hydrogen bonding interactions. At the driest environments used, healed cracks in soda-lime-silica glass required 1.7 ± 0.2 J/m² to reopen. This bonding energy can be attributed to either the formation of cationic bridges or siloxane bonds between fracture surfaces. Since crack healing is independent of the number of cycles, the cationic bridging model, which involves electrostatic interactions, is favored to explain healing effects at room temperature.

Crystallization of Sol-Gel Glasses

J. E. Blendell and J. B. Blum¹

¹Rutgers University

Many ceramics have been produced by sol-gel techniques at lower temperatures than is possible with conventional powder processing. However, the crystallization process is difficult to control to achieve the proper

crystalline phase assemblage. Controlled nucleation was used in an effort to make crystalline quartz via sol-gel techniques, to produce a tough transparent ceramic that may replace for glass in high performance applications. Heretofore, high-density polycrystalline quartz has only been produced under hydrothermal conditions. When powders are sintered in air at high temperature cristobalite forms, while at low temperature no densification occurs. Dense SiO_2 glasses can be made by sol-gel processing, and if the desired phase can be nucleated it would be possible to produce polycrystalline quartz. Nuclei were introduced during sol-gel processing of silica glass in collaboration with Prof. John Blum of Rutgers University. These sol-gel glasses with differing amounts of quartz seed (2-10 percent by weight) were heat treated over a range of temperatures. At 1000 °C cristobalite begins to form in less than a day. At lower temperatures (850-950 °C) the quartz phase begins to grow, but the kinetics are slow. Annealing for times up to 3 weeks at 900 °C leads to a small increase in the amount of quartz present as determined by x-ray diffraction. No other phases are detected. Much longer annealing times are required to determine whether fully crystalline quartz will be produced.

Ba/Ti Ratio Measurement

J. E. Blendell and R. F. Fleming¹

¹Center for Analytical Chemistry

Gamma-ray spectroscopy was used to measure the Ba/Ti ratio in compounds having the $\text{BaTi}_5\text{O}_{11}$ structure in collaboration with Ron Fleming of the Center for Analytical Chemistry. The samples were found to be Ti rich, that is $[\text{Ti}]/[\text{Ba}] > 5$. This implies that a substantial concentration of defects must be present in order for the sample to have the $\text{BaTi}_5\text{O}_{11}$ structure. Such defects are thought to be responsible for the excellent microwave dielectric properties of other high Ti compounds in the Ba-Ti system. It is possible that these defects will lead to temperature independent dielectric properties in the 1:5 material.

Research and development in ceramics for structural, optical, electronic, magnetic, and other applications is being directed increasingly toward improvements in processing science that will permit reproducible production of defect-free materials. This goal requires extremely sophisticated microstructural control. It is now recognized that the evolution of microstructure begins at the very earliest stages of processing, in the chemistry of powder synthesis, and is carried forward in subsequent compaction and densification to finished ceramic bodies. New approaches to ceramic synthesis are evolving, based on advanced molecular-level synthetic, mechanistic, and structural chemistry. Low-temperature synthetic procedures, such as the "sol-gel" processes, are becoming increasingly important for synthesis of advanced materials, often in heretofore unattainable compositions. Advanced structural techniques, such as SANS and high-resolution electron microscopy, are being utilized increasingly to elucidate the pathways by which molecular structures evolve into ceramic structures and microstructures.

The program of the Ceramic Chemistry Group is focused on research to facilitate the application of modern chemical techniques and understanding to improved processing of ceramics. The Group's goal is essentially to put more and better chemistry into ceramic processing. The objectives of the group are to provide data, measurement methods, concepts, and standard materials relating to chemical aspects of ceramics processing needed by industry for predictive control of new processes and development of new materials. Current emphasis is on advanced synthetic methods, evolution of structure in ceramic synthesis, and relation of chemical process variables to particle characteristics and microstructure.

Representative Accomplishments

- Preparation of micron particle size powder of TiB_2 using a novel low temperature synthesis method for non-oxide compounds. A patent application has been filed.
- Determination of the evolution of pores (including pore size and size distributions) in Spinel ($MgAl_2O_4$) "green" compacts and sintered materials by small angle neutron scattering (SANS).

Low Temperature Synthesis of Ceramic Powders

J. J. Ritter, K. G. Frase, N. K. Adams

Synthesis of ceramic powders using molecular level reactions at low temperature offers a number of advantages over conventional high temperature processing. The starting reagents can be highly purified, and thus enhanced product purity can be achieved. Dispersing the reagents in a solvent provides mixing on the molecular level, rather than at the particulate level as in solid state reaction. This molecular mixing increases homogeneity and

also affects the crystal structure. Powders prepared by low-temperature routes are frequently fine-grained and more reactive than those prepared conventionally, permitting reduction in sintering temperatures. Finally, metastable compounds with particularly interesting properties not accessible by solid state reaction can be often formed. Several new low temperature synthetic methods have been developed for both oxide and non-oxide materials.

The high purity and homogeneity available via low temperature synthesis have proved useful in the production of standard reference materials for instrument calibration. Submicron particles of TiO_2 have been produced with a homogeneous doping of 1 to 3 weight percent heavy metal (e.g. Zr, U, Pb) by controlled hydrolysis of alkoxide precursors. These are being evaluated as calibration standards for analytical microscopes. Particle size distribution can be controlled through the manipulation of the hydrolysis reaction parameters.

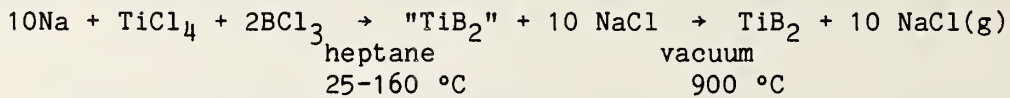
The effects of molecular level mixing and low temperature synthesis on crystallization product have been demonstrated in two ionic conductor systems, sodium beta/beta"-alumina and Y_3TaO_7 . In both systems, the final crystalline materials produced by alkoxide synthesis differ from the products of solid state reaction.

In sodium beta/beta"-alumina, solid state reaction at temperatures above 1500 °C is required to reach the equilibrium phases, which are binary beta alumina and ternary sodium beta"-alumina (Mg-stabilized). By contrast, alkoxide synthesis of materials with the beta"-alumina composition yield crystalline products at 1100 °C which have a distorted "solid solution" beta-type structure. The primary difference between the beta" and solid solution beta structures is the Mg-substitution in the aluminum-oxygen layers. In the beta" structure, this substitution is ordered (1), while in the solid solution beta structure it is random. Thus the molecular mixing inherent in alkoxide synthesis appears to favor the higher symmetry, disordered structure.

This preference for higher symmetry through alkoxide synthesis is also observed in the case of Y_3TaO_7 . When prepared by solid state reaction, Y_3TaO_7 forms as a distorted pyrochlore at temperatures between 1500 and 1700 °C. Above 1700 °C a cubic fluorite structure, like that of the oxygen ion conducting cubic zirconia, forms which can be quenched into lower temperatures. However, when prepared by alkoxide hydrolysis, the Y_3TaO_7 material begins to crystallize as the cubic phase at temperatures as low as 1000 °C. The tendency for disordered phases to form during low temperature synthesis may lead to a new group of oxide ion conductors based on "high temperature" disordered crystal structures.

Metal alkoxide chemistry is inappropriate for the synthesis of non-oxide materials. Except for the polycarbosilane and aminosilane methods for SiC and Si_3N_4 , the low temperature synthesis of non-oxide materials is largely unexplored. Other chemistries are needed to synthesize fine powders of materials such as TiB_2 and B_4C .

A novel low temperature synthesis of these non-oxide compounds adapts the Wurtz-Fittig reaction, common in organic chemistry. Metal chlorides react with sodium in a non-polar solvent to produce an amorphous precursor powder and NaCl. The NaCl can be distilled off and the precursor crystallized at temperatures as low as 900 °C:



It is proposed that the initial reaction involves halogen abstraction from each of the metal halides and a coupling of the resultant products:



Further halogen abstraction and coupling reactions generate a three-dimensional B-Ti precursor matrix denoted as "TiB₂" in the above equation. Titanium carbide and B₄C have been generated from TiCl₄, BCl₃ and CCl₄ in similar reactions.

Pore Size and Size Distribution in Spinel

K. A. Hardman-Rhyne, K. G. Frase

The problem of measuring the evolution of pore size distribution during sintering has long challenged material scientists. A non-destructive small-angle neutron scattering (SANS) technique, sensitive to defects (size up to 3 μm) and their size distribution has been developed at NBS and applied to porosity by K. A. Hardman-Rhyne and K. G. Frase.

SANS has been used to examine the sintering process using both unfired compacted powder samples ("green" ceramics) with 50 percent porosity and sintered materials with 2 percent porosity (generally consisting of closed pores). Both volume fraction and pore size (~1.0 μm) are much larger than can be seen with traditional single particle diffraction techniques in small angle scattering. Multiple scattering techniques have been developed at NBS and employed to elucidate microstructural information including pore size, size distribution, porosity, and surface areas. The analysis procedure utilizes the strong wavelength dependence of the small Q incoherent multiple scattering data to determine the scattering radius of curvature, r_c at Q=0. In addition, a Porod analysis is used to determine the total surface area of the pores from the large Q data. The SANS results are compared to data from other techniques such as SEM, mercury porosity, and BET, in which closed porosity is not detected.

Compacts of submicron spray-dried spinel (MgAl₂O₄) powder (approximately 0.76 μm in size) were uniaxially pressed at 69 GPa and then isostatically pressed at 207 GPa. The "green" pressed disks were calcined at 700 °C to remove organic binders and will be referred to as the "green" state (G.S.) sample. One G.S. sample was fired at 1300 °C for 12 hours to obtain a partially sintered material, referred to here as the sintered sample.

The small-Q regime of the scattering curves were fitted to a Gaussian function and the incident beam scattering was subtracted to obtain $r_c[Q]$ (the notation means radius of curvature at the origin in Q units) as a function of wavelength. The $R_{eff}(0)$ or effective void radius measured from the small-Q data for the G.S. and sintered samples is 400 and 800 nm, respectively. The $R_{eff}(\infty)$ or effective void radius measured by the large-Q data and surface area of the voids was determined from the analyses of the Porod regime. The $R_{eff}(\infty)$ for the G.S. sample is 160 nm and for the sintered material, 690 nm. The surface area for the G.S. sample is $4.5 \text{ m}^2/\text{gm}$, which is in good agreement with gas adsorption results.

The two R_{eff} values obtained for the "green" state could suggest a distribution of void sizes, but the large difference here suggests that two different size characteristics are being measured; that of "neck" and "bottles" of ink-bottle type connected porosity. In the sintered material the SANS measures both closed and open porosity. With the completion of the cold source at the reactor this year, higher wavelengths will be available which will allow measurements of pores or inclusions up to $30 \text{ }\mu\text{m}$. This is particularly significant in that the size range of 5 to $30 \text{ }\mu\text{m}$ will allow SANS results to be compared with other NDE techniques such as thermal waves and ultrasonics which can be used as sensors for on-line process control.

Structural Evolution in Low-Temperature Ceramic Processing

T. D. Coyle, K. Hardman-Rhyne

Although low-temperature synthesis of ceramic powders and glasses offers numerous advantages, its use has been largely empirical. A new research program has been initiated to elucidate the fundamental reaction mechanisms by which structure evolves in low temperature processing from molecular precursors to glass or crystalline products in multicomponent systems. The objective of the work is to define the critical chemical parameters that will permit predictive control of powder, film and glass processing. Current research emphasizes processes for synthesis from metal-organic precursors of multicomponent oxide-systems of interest as electronic or dielectric materials. Molecular structure and kinetics are being studied spectroscopically (FTIR, NMR); the polymerization of molecular species to amorphous ceramic precursors and densification of sol-gel derived materials is being evaluated by SANS methods; and crystallization of amorphous precursors is being studied by conventional x-ray diffraction techniques.

A project has been initiated in cooperation with the Ceramic Characterization Group to prepare silica powders (doped at low levels with alkalis, alkaline earths, and transition elements) from alkoxide precursors and to investigate crystallization behavior of these. The objective is to understand the effects of dopants on crystallization of sol-gel derived amorphous silica and to generate crystalline tridymite-containing materials for application as quantitative x-ray powder diffraction standards for quality control in the refractories industry and for use in environment measurements. Amorphous silica powders with highly uniform particle size in the 0.2 micron range (which may be useful as SEM resolution standards) have been obtained, and doping and crystallization studies are in process.

Collaborative work with MIT has begun on concentrated colloidal suspensions using small angle neutron scattering; this represents an area that will be expanded in the future.

OUTPUTS AND INTERACTIONS

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SELECTED TECHNICAL/PROFESSIONAL COMMITTEE LEADERSHIP

American Ceramic Society

Committee on Publications

Subcommittee on "Phase Diagrams for Ceramists"

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Glass Division

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1985 Annual Meeting Local Arrangements Committee
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INDUSTRIAL AND ACADEMIC INTERACTIONS

In 1985, the Division performed collaborative research with over 50 private organizations through its Industrial Research and Guest Worker programs and other joint arrangements. Representative examples of such interactions include:

INDUSTRIAL

1. AT&T Bell Laboratories

Research on the crystallographic characterization of ionic ceramic conductors is being carried out in a collaborative program between R. J. Cava and D. W. Murphy of Bell Laboratories and A. Santoro (Reactor Division) and R. S. Roth. Lithium inserted oxides are prepared at Bell Labs and characterized at NBS using the neutron diffraction total profile (Rietveld) analysis. The neutron diffraction data and analysis techniques uniquely locates the position of the lithium ion in the structure. Current emphasis of the joint work is on alkali niobium-tungsten-vanadium oxide phases having the pyrochlore type structure.

2. Atlantic Mining Company

The Surface Chemistry and Bioprocessing Group is carrying on a research collaboration with AMC to characterize biological processes potentially useful for recovery of previous and strategic metals from certain major domestic deposits, low grade pyritic ores. These ores are not amenable to conventional processing due to matrix effects and low grade nature of the deposits. In addition to selective bioextraction of noble metals, platinum and gold for example, new bioreactor designs are being evaluated for improving iron processing.

3. Battelle Memorial Institute

B. Steiner has worked closely with Battelle Memorial Institute in identifying areas for close technical collaboration in support of a multiclient program that Battelle is assembling to develop electrooptic technology for optical communications. Initial research has begun in collaboration with the Center for Analytical Chemistry in the analysis of single crystals of lithium niobate. Parallel synchrotron topographic studies will be initiated shortly.

4. Crystal Technology, Inc.

B. Steiner and the Synchrotron Group of the Metallurgy Division have collaborated with Crystal Technology on monochromatic topographic examination of specially grown lithium niobate single crystals during the first two weeks of dedicated x-ray ring operation at the National Synchrotron Light Source. Crystals grown under various conditions display highly growth-dependent defects and strains. Such defects can affect the fabrication of complex communications and computing

devices made from these crystals. Correlation of the topographic information with parametric variation in the crystal growth process will help to separate those defects associated with the initial crystal growth from those associated with subsequent diffusion to form waveguides in the crystal.

5. Cummins Engine Company

Cooperative research between the Tribology Group and Gordon Starr (Cummins) involves ceramic tribology related to heat engine development. Research centers on the mechanism of failure, surface topography effects, and microstructural influence on wear of ceramic coatings and parts.

6. General Motors

Cooperative research between N. Hakim (GM) and S. Hsu is being carried out on the lubrication mechanism of ceramic parts in engine contacts.

7. American Ceramic Society
(Ceramics Industry)

The High Temperature Chemistry Group interacts with the Ceramics Industry, through the Joint NBS/ACerS Phase Diagrams for Ceramists Program. The ceramics industry provides information to NBS on phase diagram needs and priorities through their participation in ACerS-NBS Committees and through direct interactions (visits) between industrial and NBS management and technical personnel. The industry is also funding a Ceramic Society program for Research Associateships to expand the NBS Data Center on ceramic phase diagrams. The Ceramic Society publishes and disseminates the Data Center outputs which have included five hard-cover volumes containing 6500 evaluated phase diagrams, and which in the future will also include on-line computer services to industry.

8. American Iron and Steel Institute (AISI) and Cleveland Cliffs Iron Company

The Surface Chemistry and Bioprocesses Group is collaborating with Cleveland Cliffs Iron Company (William Hancock, Research Coordinator) in examining upgrading of ores and concentrates via biological phosphorus, silicon, and sulfur removal.

9. Joint Committee for X-ray Powder Diffraction Standards
(JCPDS)--International Centre for Diffraction Data

For nearly 30 years this cooperative program with industry (JCPDS) has served as the focal point for the provision of high quality reference powder patterns for inclusion in the JCPDS's Powder Diffraction File. Under an expanded relationship with JCPDS, the program at NBS now includes critical evaluation of published data, development of a numerical data base, and research on producing accurate data and on the use of these data in phase identification.

The JCPDS publishes the well known Powder Diffraction File, the oldest numerical data compilation for analytical purposes in the world (over 20 different publications covering powder and single crystal diffraction data are offered). The Ceramic Powder Characterization Group provides overall technical guidance to the research associates sponsored by JCPDS in the provision of reference patterns; promotes and coordinates the activities of the research associates with other data centers; and develops standard reference materials for calibration of x-ray diffraction equipment. The JCPDS disseminates the data through numerous mechanisms.

JOINT INDUSTRIES/UNIVERSITIES

1. AT&T Bell Laboratories, Trans Tech Division of Alpha Industries, University of Pennsylvania and Arizona State University

A joint program on dielectric ceramics having important microwave applications is being carried out by R. S. Roth, J. J. Ritter, W. Coblentz, and J. Blendell in association with R. J. Cava, H. O'Bryan (Bell Labs), T. Negas (Alpha Industries), P. Davies (U. of Pennsylvania) and A. Olsen (Arizona State U.). Powders of barium poly-titanates (pure and doped) are synthesized from alkoxide precursors, conditioned, compacted and densified at NBS with phase equilibria and crystal chemistry determined at each processing step. Characterization of microwave properties (dielectric constant, Q, TCK, etc.) is performed on NBS prepared powders and compacts by the Industrial organizations. The University groups investigate the materials using high resolution electron microscopy lattice imaging techniques, correlating observed and calculated lattice image defects with the dielectric and thermodynamic properties.

2. General Electric and Rice University

NBS participates in a joint program with NASA for materials processing in space. D. W. Bonnell (High Temperature Processes Group) plans, supervises, and participates in experiments jointly with personnel from GE and Rice University at the King of Prussia laboratory (PA). These experiments involve use of a state-of-the-art facility designed by Dr. Bonnell for levitation melting of tungsten and other refractory metals coupled with drop calorimetry. The results, in addition to providing basic thermodynamic information indicate the limitations of ground-based versus space experiments.

UNIVERSITIES

1. Johns Hopkins University

Robert Kelly of the Chemical Engineering Department and G. J. Olson and F. E. Brinckman are conducting joint research on microbial attachment to and solubilization of strategic metal ores characterized by non-destructive surface analysis techniques including epifluorescence microscopy and FTIR.

2. Massachusetts Institute of Technology (MIT)

Joint work with R. Coble (MIT), C. Handwerker (Metallurgy Division), J. Blendell, K. Rhyne, and K. Frase, involves the characterization of flaws (pores) in alumina ceramics, by SANS and conventional microstructural techniques. Samples having different porosities are prepared at MIT and analyzed at NBS with the goal of correlating pore size distributions with SANS data; an important result will be the effect on pore size distribution caused by polishing and etching.

3. Northwestern University

Joint research involves lubrication modeling between S. Hsu and Prof. Herbert Cheng. The research focuses on the microelastohydrodynamic theories under wearing conditions. This is the first attempt at combining surface chemistry with surface mechanics to create a predictive wear model.

4. Pennsylvania State University

The Phase Diagrams for Ceramists Data Center has an ongoing contractual/collaborative interaction with K. Spear of the Materials Science Department. He is developing the mathematical basis and computer software for including NBS developed solution models into phase diagram optimization/prediction codes. At the present time, existing computer codes for phase diagram modeling, developed for relatively simple alloy and molten salt systems, are not applicable to the more complex ceramic systems, e.g., oxides. This technical advance is necessary to the successful implementation of the NBS/ACerS five year development program for a computerized ceramic phase diagram data base.

The Tribology Group has several joint research projects with the Department of Chemical Engineering and the Materials Research Laboratory at PSU. The principal collaborators are S. Hsu, R. Munro, and R. Gates of NBS and Prof. E. Klaus, Prof. L. Duda, Prof. N. Macmillan, D. Deckman, and J. Yellets of PSU. The research projects include fundamental studies on the vapor phase lubrication of ceramic materials at high temperature; microstructural effects in ceramic wear processes; high temperature friction and wear tribometer design; and ceramic wear modeling which seeks to establish a theoretical understanding of ceramic wear processes.

5. Rensselaer Polytechnic Institute

G. J. Olson and F. E. Brinckman are collaborating with Professor Henry L. Ehrlich on mechanisms of silver ore solubilization and resistance in metal ore processing bacteria.

6. Rice University

D. W. Bonnell interacts with J. L. Margrave of the Chemistry Department at Rice University for the purpose of developing (and applying) state-of-the-art levitation calorimetric techniques. These techniques are needed for the determination of basic thermodynamic

quantities of refractory materials (e.g., W, Ta, carbides) in their solid and liquid states. The collaborative effort is sponsored by the NASA Materials Processing in Space Program, and General Electric is a third member of this Government-University-Industry team.

7. Rutgers University

Joint work with J. Blum (Rutgers) and J. Blendell involves production of seeded sol-gel glasses to be used in studies of phase controlled crystallization at NBS.

8. University of California, Lawrence Livermore National Laboratory

Joint work with M. Weber (LLNL) and D. Blackburn and W. Haller involves the luminescent behavior of various elements in glass matrices. Matrix composition and processing conditions affect such parameters as emission wavelength, band width, life time and quantum yield which are of importance to glass lasers and optical frequency convertors. Oxide and non-iron-oxide glasses with emitting elements are developed at NBS and characterized for glass forming and element loading capability. LLNL measures optical parameters, and the results are correlated to glass composition. The goal of this work is to improve the understanding of luminescence and may lead to novel types of lasers.

In another joint work between NBS and LLNL, W. Haller collaborated with T. Bernat, D. Miller and other members of LLNL in the development of high pore volume aerogels. Aerogels of this type are used to study equation of state behavior under extreme conditions.

9. University of Cincinnati

Scientific collaboration with Prof. John S. Thayer on molecular mechanisms of metal solubilization and transformation by biogenic metabolites is being pursued. G. J. Olson and F. E. Brinckman are co-authoring patent with Thayer on using biogenic methyl iodide as a novel metal ore extraction process.

10. University of Maryland

Members of the Surface Chemistry and Bioprocesses Group are collaborating with Prof. Michael Bellama and his doctoral students on biological and chemical transformations of organometallic materials in environmental situations.

J. Iriate of the University of Maryland and J. Ritter have been collaborating on problems related to the synthesis of barium titanates precursors from mixed alkoxides. The work is important to the industrial development of ceramics having tailored properties for microwave applications. Specifically, the joint investigation is designed to isolate and characterize the intermediate reaction products which occur during synthesis. The information gained from these studies will improve the understanding of the chemistry and structure that persist when alkoxides are mixed and how these factors influence the development of the precursors upon hydrolysis.

11. University of Minnesota

Cooperative research is underway between S. Hsu and Prof. Ramalingam on ceramic coating and coating evaluation for advanced technological concepts.

12. University of New Hampshire

The Surface Chemistry and Bioprocesses Group is collaborating with Prof. Richard H. Blakemore on in vivo characterization of metal particle formation rates and sites in magnetite-depositing bacteria, using SANS characterization. G. J. Olson, F. E. Brinckman, and K. Rhyne are participating in the research.

13. University of Southern California

B. Steiner and the Synchrotron Group of the Metallurgy Division have collaborated on monochromatic topographic examination of bismuth silicon oxide crystals during the first two weeks of dedicated x-ray ring operation at the National Synchrotron Light Source. These crystals display highly growth-dependent defects and strains associated with the detailed character of the crystal growth. Such defects can affect the performance of signal processing devices made from such crystals. Correlation of the topographic information with parametric variation in the crystal growth process will help to identify those aspects of growth that most critically affect device performance.

14. University of Tennessee Space Research Institute (UTSI)

UTSI functions are primarily of an industrial R & D nature. Their interaction with NBS has been long standing and revolves around their development of coal fired MHD systems and their need for NBS basic data and models of the MHD slag behavior. UTSI provides (E. Plante) with slag samples from their pilot plant tests, and NBS carries out basic vaporization and phase equilibria measurements on these samples. The results are used by UTSI and also by J. Hastie and D. Bonnell to develop predictive models of slag thermochemistry under actual MHD use conditions. NBS recently completed development of a highly successful model, which is now in use by Lloyd Crawford of UTSI. This model can predict the vaporization, seed retention, and phase equilibria behavior of complex MHD slags containing oxides of Na, K, Ca, Mg, Al, Si, and Fe.

15. Virginia Polytechnic Institute and State University

Cooperative research between Prof. Larry Taylor (VPI). P. Pei, and K. Jewett investigates surface reaction product analysis under wearing conditions.

16. Washington University

G. Olson and F. Brinckman are collaborating with Prof. Simon Silver on the molecular biology of metal resistance and transformations in commercially applied metal ore processing bacteria.

STANDARD REFERENCE MATERIALS

The Division provided science, industries, and government a central source of well-characterized materials certified for chemical composition of physical or chemical properties. These materials are issued with a certificate and are used to calibrate instruments, to evaluate analytical methods, or to produce scientific data which can be referred to a common base.

<u>DESCRIPTION</u>	<u>SRM NUMBER</u>
Alumina Elasticity	718
Alumina Glass Anneal Point	714
Alumina Glass Anneal Point	715
Alumina Melting Point	742
Aluminum Magnetic Susceptibility	763-1
Aluminum Magnetic Susceptibility	763-2
Aluminum Magnetic Susceptibility	763-3
Barium Glass Anneal Point	713
Borosilicate Glass Composition	93(A)
Borosilicate Glass Thermal Expansion	731L1
Borosilicate Glass Thermal Expansion	731L2
Borosilicate Glass Thermal Expansion	731L3
Cadmium Vapor Pressure	746
Container Glass Composition	621
Container Glass Leaching	622
Container Glass Leaching	623
Copper Thermal Expansion	736L1
Fused Silica Thermal Expansion	739L1
Fused Silica Thermal Expansion	739L2
Fused Silica Thermal Expansion	739L3
Glass Dielectric Constant	774
Glass Electrical Resist	624
Glass Fluorescence Source	477
Glass Liquidus Temperature	773
Glass Refractive Index	1820
Glass Sand (High Iron)	81A
Glass Sand (Low Iron)	165A
Glass Stress Optical Coefficient	708
Glass Stress Optical Coefficient	709
Gold Vapor Pressure	745
High Boron Glass Viscosity	717
Intensity XRD Set	674
Lead Barium Glass Composition	89
Lead Glass Anneal Point	712
Lead Glass Viscosity	711
Liquids Refractive Index	1823
Low Boron Glass Composition	92
Lube Oil Oxidation Test Kit	1817
Lube Oxidation Catalysts	8500

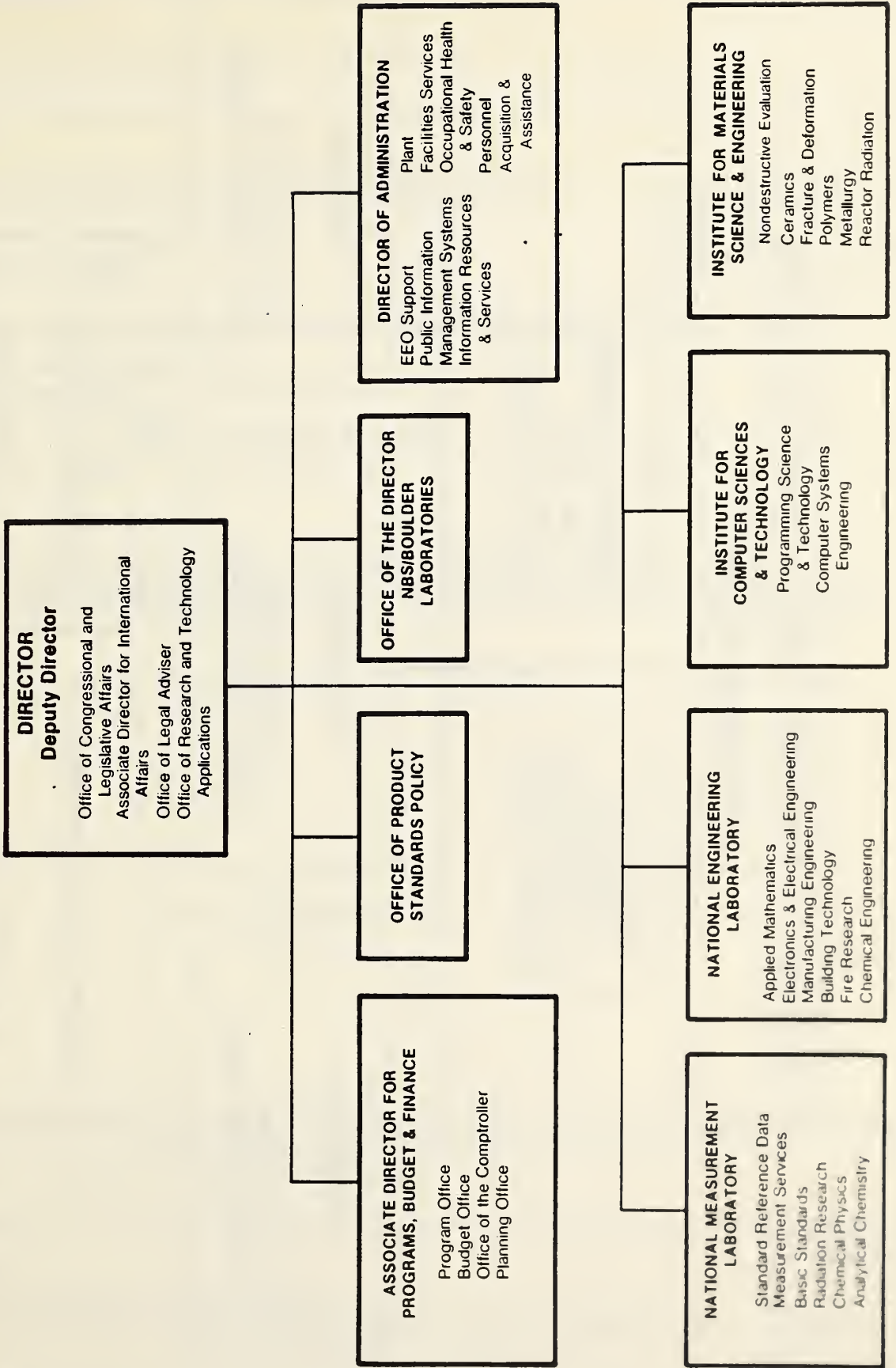
MNF ₂ Magnetic Susceptibility	766-1
Mica X-Ray Diffraction	675
Neutral Glass Anneal Point	716
Nickel Magnetic Susceptibility	772
Opal Glass Composition	91
Palladium Magnetic Susceptibility	765-1
Palladium Magnetic Susceptibility	765-2
Palladium Magnetic Susceptibility	765-3
Platinum Magnetic Susceptibility	764-1
Platinum Magnetic Susceptibility	764-2
Platinum Magnetic Susceptibility	764-3
Refractive Index Glass	1822
Respirable Quartz	1878
Ruby EPR Absorption	2601
Sapphire Thermal Expansion	732
Silicon X-Ray Diffraction	640(A)
Silver Vapor Pressure	748
Soda Lime Flat Glass Composition	S620
Soda Lime Float Composition	1830
Soda Lime Glass Viscosity	710
Soda Lime Sheet Composition	1831
Toluene 5 ML	211C
Tungsten Thermal Expansion	737



APPENDIX



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Document describes a computer program; SF-185, FIPS Software Summary, is attached.

11. ABSTRACT (A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here)

Current programs of Ceramics Division are reviewed.

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