UNIVERSITY OF WASHINGTON

College of Engineering

Ceramic Engineering Division

Multidisciplinary Research Activity in the Materials Sciences with Emphasis on Ceramic Materials

NASA Research Grant Number NsG-484

Semiannual Status Report Number 8
December 16, 1966 through June 15, 1967

James I. Mueller, Professor
Ceramic Engineering
Principal Investigator

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INTRODUCTION

The Ceramic Materials Research Program at the University of Washington was established June 1, 1963, under National Aeronautics and Space Administration Grant Number NsG-484. The principal purposes of the grant are to encourage multidisciplinary research upon the nature and properties of ceramic materials and to assist this institution in the development of an enduring research capability in ceramics and ceramic engineering. The funds are, therefore, used to make financial support available for research on ceramic materials conducted by members of the University faculty and to purchase such items of capital equipment as are deemed desirable for the implementation of the stated purposes.

The program, planned to study the effects of various energy environments upon ceramic materials, is divided into several broad research areas, namely; chemical, surface phenomena, solid state ceramics and processing. The research program is planned and coordinated by the Ceramic Materials Research Committee, the membership of which is appointed by the Dean of the Graduate School. The current membership includes James I. Mueller, Ceramic Engineering, Chairman and Principal Investigator; Norman W. Gregory, Chemistry; John L. Bjorkstam, Electrical Engineering; O. J. Whittemore, Jr., Ceramic Engineering; and Barry D. Lichter, Metallurgical Engineering. Administration of the program is coordinated by a board consisting of E. C. Lingafelter, Associate Dean of the Graduate School, Chairman; D. E. McFeron, Chairman, Committee on Research Policy, College of Engineering; D. A. Pifer, Director of the School of Mineral Engineering and James I. Mueller, Principal Investigator.

GENERAL PROGRAM REPORT

This is the eighth semiannual status report and covers the second half of the fourth year of operation under this grant. During the report period, a total of twenty projects were supervised by fifteen faculty members in five academic disciplines of the University. A tabulation relating academic departments to research areas and to the number of individuals receiving support will be found in Appendix A. The number of projects appears to be reduced from the last report, but most of this is due to the consolidation of projects, accomplished to facilitate administration of the program.

The Ceramic Materials Research Seminar, a period devoted to discussions of concepts and research of interest to the program, met for a total of sixteen sessions during the past six months. The speakers included four graduate students, four University faculty members and eight visitors. The latter included Dr. Terry D. Gulden, General Atomics; Dr. Robert G. Lye, Research Institute of Advanced Studies, Martin Company; Dr. M. H. Kamdar, Research Institute of Advanced Studies, Martin Company; Mr. D. R. Gaskell, McMaster University; Mr. George McLellan, Corning Glass Works; Mr. Larry D. Riley, Tektronix, Inc.; Dr. H. B. Probst, Lewis Flight Center and Mr. Dean Carey, Tektronix, Inc.

The discussion group program was expanded as those faculty members and students studying upon the solid state aspects of ceramic materials initiated bi-weekly meetings to discuss research areas of mutual interest. The chemical group continued their discussion of research on the zirconium-oxygen-carbon system. The program supported the attendance of eight faculty members to a total of four technical meetings of which four papers were presented based upon work supported by the grant. Papers published or presented resulting from work supported wholly or in part by the grant are listed with the individual status reports and in Appendix C.

The NASA Technical Monitoring Committee, consisting of Mr. James J. Gangler, Chairman, Dr. Martin H. Leipold and Dr. H. B. Probst, made their annual visit on May 16, 17 and 18, 1967. The project supervisors presented short briefings on their research on the first morning, after which the committee members visited each supervisor and his research staff in their laboratories.

Professor Mueller was invited to participate in the review of the solid state research program at the Research Institute for Advanced Studies, Martin Company, Baltimore, on April 27, 1967.

RESEARCH STAFF

Faculty Supervisors:

J. L. Bjorkstam, Ph.D.
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D. W. Nevin, Engineering Assistant

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STUDIES OF THE ZIRCONIUM-OXYGEN-CARBON SYSTEM

This system has been selected as the subject of a general study of the effects of the chemical environment upon ceramic materials. Several faculty members from various disciplines are participating in a coordinated study to obtain basic knowledge regarding this system.

GAS-SOLID EQUILIBRIUM

James I. Mueller
Professor, Ceramic Engineering

The composition and pressure of the gaseous phase(s) associated with the solid phases at various temperatures materially affects the equilibrium of a system. It is the purpose of this research to study the effects of these variables upon the Zr-O-C system.

Thermochemical Study of Zirconium Oxy-Carbide

A. D. Miller
Predoctoral Associate, Ceramic Engineering (December 16 to June 15)
Ph.D. Thesis Research

The objective of this study is the determination of the existence and selected properties of a proposed ternary compound of approximate composition $ZrO_{0.5}C_{0.5}$ in the system Zr-O-C. A dual approach to the problem is being followed. First, an investigation of the electronic band structure and its relationship to bonding properties, and second, a thermochemical study of the solution of oxygen in the ZrC phase.

The band structure studies were completed during this report period. Band structures and density of states curves were calculated for nine compositions along a pseudo binary ZrC-ZrO. These studies indicate that the compositions near $ZrO_{0.5}C_{0.5}$ are qualitatively similar to ZrC in that no band gap exists and thus these compositions should be metallic conductors. Rough calculations of the cohesive energy of the $ZrO_{1-x}C_x$ compositions show a minimum in the range $0.6<x<0.8$.

Experimental work continued on equilibration of ZrC with oxygen containing atmospheres. Experiments conducted over a temperature range of 1100-1500°C at oxygen pressures ranging from 10^{-6} to 10^{-7} atm yielded no products which can be identified as the proposed ternary compound. The temperature and oxygen pressure variables have not been independent, however, the lowest oxygen pressures having been only achievable at the lowest temperatures. Modifications in the experimental design will have to be made in order to continue this problem.

Studies of the Zirconium Dioxide-Carbon Reaction

S. K. Sarkar
Predoctoral Associate, Ceramic Engineering (December 16 to June 15)
Ph.D. Thesis Research

Previous work has indicated the evidence of a consensed phase, tentatively identified as $ZrO_{0.5}C_{0.5}$. The purpose of the continuing study is: (1) to obtain additional information upon the nature of the reactions involved, and (2), to make initial characterization of the material.

Studies to determine the initial requirements of the reaction indicate that, in a carbon tube furnace under 10^{-4} Torr vacuum, none of the proposed ternary phase is produced at temperatures less than 1500°C. A face-centered cubic phase other than ZrC has been identified at reaction temperatures between 1500°C and 1900°C. Work with the high temperature x-ray furnace using either a tantalum or a carbonized tantalum sample holder-resistance elements has resulted in the formation of a tantalum zirconate. However, studies are continuing with the x-ray furnace using lower vacuums and higher carbon contents to observe the formation of zirconium oxy-carbide in the presence of the tantalum zirconate reaction.

A furnace with a carbon heating element has been assembled to permit the use of a known carbon monoxide atmosphere and experimentation will continue.

Influence of Oxygen Activity on the Structure of Zirconium Oxide

K. M. Nair
Predoctoral Associate, Ceramic Engineering (December 16 to June 15)
Ph.D. Thesis Research

The purpose of this study is the determination of the effects of low oxygen partial pressure at high temperature upon the stability of ZrO_2. It is planned to study the possible existence of lower oxides of zirconium, their dependence upon oxygen activity and temperature, and the influence of the formation of such an oxide upon the formation of a ternary compound in the Zr-O-C system.

No stable oxides of zirconium lower than ZrO_2 have been observed in the equilibrium study of Zr-O systems for temperatures ranging between 700°C and 1600°C and oxygen partial pressures of range log oxygen pressure = 10^{-14} and log oxygen pressure = 10^{-2}. It has been observed, however, that the color of "ZrO_2" varied from black through shades of gray to white with increasing oxygen pressures. These "black oxides" changed to a white color when heated in air or oxygen. The diffraction line intensities and the d-spacings of the x-ray powder patterns increases with some consistency with the increase of oxygen-partial pressure. It has also been noted that a discontinuity exists in the temperature versus d-spacing plot at the monoclinic-tetragonal transformation region.

Work is proceeding to determine the relationship of color and oxygen deficiencies and the non-equilibrium study of Zr-O systems for varying temperatures and oxygen partial pressures.

SOLID-SOLID EQUILIBRIUM

N. W. Gregory
Professor, Department of Chemistry

A thermodynamic and kinetic study of chemical reactions in oxide-carbide-graphite systems.

Effusion Study of Graphite, Metal Oxide and Metal Carbide Systems

Juey Hong Rai
Research Assistant, Chemistry (December 16 to June 15)
Ph.D. Thesis Research

This is a study of equilibrium and kinetic properties of chemical reactions between graphite and certain metal oxides and metal carbides. The reaction is followed by measuring steady-state effusion pressures of gases produced, usually CO. When equilibrium pressures can be determined, thermodynamic analysis of the result will be made.

A preliminary study of the reaction of MgO and graphite has been made. Mg vapor and CO are formed. The total pressure appears about 100 times less than expected from JANAF data; equilibrium may not have been reached. Effects of orifice dimensions, pellet pressing and of possible catalytic additives are to be studied. A preliminary study of reaction of ZrC and MgO has also been made. CO and Mg vapors are released; steady state pressures are maintained for reasonably long periods and seem near expected equilibrium values; however, calibration of the apparatus has yet to be confirmed so no definite results can be given at this time.

CALORIMETRIC INVESTIGATION OF CERAMIC AND RELATED MATERIALS

Barry D. Lichter
Associate Professor, Metallurgical Engineering

The objectives are the construction of a high-temperature diphenylether drop calorimeter and the study of heat capacity and heats of transformation of ceramic and related materials.

High-Temperature Drop Calorimetry

Hugo W. Schimmelbusch
Research Assistant, Metallurgical Engineering (December 16 to June 15)
M.S. Thesis Research

All components of the high temperature tube furnace have been acquired and manufactured. Construction of the calorimeter supporting members, counterweight system and calorimeter gates has been completed. The dropping mechanism design refinements and its construction are underway.

The gravimetric system is under design at present. Purification of diphenylether has been completed. The constant temperature thermostat for control of the calorimeter receiving vessel to ±0.001°C has been checked out and found satisfactory.

THERMODYNAMICS OF TERNARY CERAMIC PHASE DIAGRAMS

Gerald W. Toop
Assistant Professor, Metallurgical Engineering

The object of this investigation is to attempt to predict phase boundaries in ternary phase diagrams using the thermodynamic properties of the binary systems.

Ternary Ceramic Phase Diagrams

Dong Nyung Lee
Research Assistant, Metallurgical Engineering (December 16 to June 15)
M.S. Thesis Research

This work is continuing by applying the method of calculation to ternary systems involving refractory metal oxides and carbides for which binary thermodynamic data is available. It has been found that a promising way of displaying and analyzing the ternary data is to assemble a three-dimensional model of the ternary integral molar free energy of mixing surface. The phase boundaries can then be determined by applying a tangent plane to the model.

Further development of the theory has shown that two of the three terms in the regular solution equation, used in the calculations, become general and rigorous near each pure component in any ternary system. This indicates that the method should give exceptional results in ternary systems in which one of the components is present as a major constituent.

ZIRCONIUM OXIDATION

Thomas F. Archbold
Assistant Professor, Metallurgical Engineering

This research project is investigating the characteristics and mechanisms of the initial stages of oxidation of zirconium metal. The oxide crystal structure and metal-oxide orientation relationships are to be determined as a function of oxygen partial pressure and temperature.

Zirconium Oxidation

L. P. Srivastava
Predoctoral Associate, Metallurgical Engineering (December 16 to June 15)
Ph.D. Thesis Research

To date, a gas train providing a variable partial pressure of oxygen (balance argon) has been used to oxidize zirconium foil specimens for periods of time ranging from 0.5 seconds to one minute at 798°C. A technique was developed to strip the oxide films from the metal for their observation in the electron microscope; published stripping techniques led to artifacts in the oxide. Present results show that monoclinic zirconia initially develops on the metal surface as thin "streaks" of oxide which are apparently related to the dislocation structure on or near the metal surface. These "streaks" later develop into, or are superceded by, a continuous and finely grained zirconia film. This growth sequence holds for metal foils oxidized at both one atm oxygen and at one ppm oxygen. The oxidation kinetics, of course, change with oxygen pressure. Similar studies are now being carried out at 500°C, and a third temperature will be selected. The orientation characteristics of the stripped oxides are being studied by the use of electron diffraction but the exact details are difficult to analyze due to the complex patterns resulting from the fine grain size. This portion of the work has been postponed temporarily until the reciprocal lattice patterns have been calculated and analyzed.

Future work will involve the correlation of structure information with kinetic data obtained by the use of the Cahn Electrobalance. It is planned to add a third component, carbon, to the system after the completion of the present project.

SOLID STATE CERAMICS

The bulk properties of some ceramic materials are of prime importance and these are, for the most part, dependent upon structural considerations. The purpose of this research is to relate the nature of crystalline ceramics with appropriate properties.

PHASE TOPOGRAPHY

Jerry E. Turnbaugh
Assistant Professor, Ceramic Engineering

Selected microstructural features common to ceramics are being studied in terms of the variables leading to their development.

Phase Topography

Pei Sung
Predoctoral Associate, Ceramic Engineering (December 16 to June 15)
Ph.D. Thesis Research

The purpose of the present work is to measure the equilibrium solubility of Helium in UO_2 and to study the growth of Helium bubbles under conditions of supersaturation.

Numerous measurements of Helium solubility and diffusivity have been made at temperatures and pressures up to 1500°C and 100-atm and work has been completed on a theoretical prediction of Helium solubility which now requires evaluation.

A paper entitled "Calculation of the Temperature-Dependent Shear Modulus of UO_2" by J. E. Turnbaugh and Pei Sung has been submitted for publication in the Journal of Nuclear Materials.

A paper entitled "Calculation of Diffusivity and Solubility with Error Analysis for Diffusion in a Sphere" by J. E. Turnbaugh and Pei Sung has been submitted for publication in the Journal of the American Ceramic Society.

DOMAIN DYNAMICS IN ISOMORPHOUS FERROELECTRICS

John L. Bjorkstam
Professor, Electrical Engineering

The objective of this investigation is to develop a microscopic model which explains essential features of the polarization reversal process in hydrogen bonded ferroelectrics of the KH_2PO_4 class.

Ferroelectric Domains and Domain Motion in KH_2PO_4 and KD_2PO_4

Richard E. Oettel
Predoctoral Associate, Electrical Engineering (December 16 to June 15)
Ph.D. Thesis Research

One of the interesting side issues of our investigation, has been the observation that 180° domains in ferroelectrics are often unaffected by the presence of shorted electrodes. Attention had been called to this unexpected phenomenon by workers in other laboratories. We have now been able to show the origin of this effect. It depends essentially upon the presence of a surface layer whose spontaneous polarization and dielectric constant are much less than that of the bulk material. A theoretical framework for determining the conditions (i.e., crystal thickness, surface properties, etc.) under which 180° domain formation is not effected by shorted electrodes, has been established. In addition, work is progressing normally on the acquisition of data related to the influence of temperature, and the degree of deuteration, upon domain velocities in the above mentioned crystals, when a step voltage is applied. It has been found that the domain velocities depend not only upon the height of the voltage step, but upon the dc biasing voltage as well. Before continuing the investigation with step voltages it has been necessary to study the influence of the biasing voltage.

In addition to contributions in understanding the basic microscopic crystal properties which limit the switching rate of ferroelectrics, our research is concerned with the general problem of domain formation and polarization reversal in ferroelectrics. Many of the proposed uses for ferroelectrics depend upon these properties.

A paper entitled "180° Domain Formation in Ferroelectrics with Shorted Electrodes" by John L. Bjorkstam and Richard E. Oettel was published in the Bulletin American Physical Society, 12, p.557 (1967).

A more complete account of this work has been accepted for publication in the July 10, 1967 issue of the Physical Review.

ELECTRON DISTRIBUTIONS AND RELAXATION TIMES

J. G. Dash
Professor, Department of Physics

Edward A. Stern
Professor, Department of Physics

Robert L. Ingalls
Assistant Professor, Department of Physics

Relations between lattice dynamics and electronic configurations in FeF_2 and $FeCl_2$, by means of the Mössbauer effect.

Charging in Alloys and Compounds: Mössbauer Examination of Silver-Tin Alloys

This experiment will measure one parameter of the electronic configuration in an alloy system that is simple enough to offer hope of making reasonably complete calculations. By measuring the electron density at the nucleus via the isomer shift one has a more stringent check on calculations than is given by checking energy levels. Some knowledge of the force constants of the lattice as a function of tin concentration is also available via the second order doppler shift. Also, there is a possibility of investigating an order-disorder transition in the ε phase.

The experimental work is just starting and a method for preparing specimen has been tried. The Mössbauer spectrometer is set up and gives good spectra with Fe^{57}.

The total velocity shift will be measured primarily as a function of tin concentration and secondarily as a function of temperature in order to separate out the changes in the isomer shift from the second order doppler shift at room temperature. There is a possibility of making the same measurements in amorphous alloys.

Anharmonic Forces in Solids

Duane P. Johnson
Predoctoral Research Associate, Depratment of Physics (December 16 to June 15)
Ph.D. Thesis Research

This study involves the use of the Mössbauer effect to explore the anharmonic force constants of Fe in various compounds. The specific interest is on the "low temperature anharmonicity" which is exhibited in several classes of materials, including ferroelectrics, high field superconductors, small ionic impurities in solids, and others.

An experimental investigation of $FeCl_2$ and FeF_2 shows that such anharmonicity is quite evident in $FeCl_2$, but not in FeF_2. This work is nearing completion, and forms the basis of Mr. Johnson's Ph.D. Thesis. As a side effect of this work, a novel sample clamping technique was developed for minimizing vibrations at low temperature. A theoretical analysis of the Debye-Waller factor of several crystal models is under way, and a manuscript is in preparation.

An experimental study of additional compounds will be undertaken along the lines of the current study.

A paper entitled "Debye-Waller Factor for FeF_2" by D. P. Johnson and J. G. Dash was published in the Bulletin American Physical Society, 12, p.378.

A paper entitled "Mössbauer Effect of Divalent Fe^{57} in NiO and MnO" by J. D. Siegwarth was published in the Physical Review, 155, p.285 (1967).

A paper entitled "A Novel Clamping Technique for a Mössbauer-Cryostat" by D. P. Johnson, G. A. Erickson and J. G. Dash has been submitted for publication in the Review of Scientific Instruments.

A paper entitled "Debye-Waller Factor for $FeCl_2$" by D. P. Johnson and J. G. Dash was presented at the American Physical Society Meeting in Chicago, Illinois, March 1967.

EFFECTS OF RADIATION UPON CERAMIC MATERIALS

James I. Mueller
Professor, Ceramic Engineering

Electromagnetic spectral radiation causes varying physical and chemical effects upon materials. The nature of the effects is usually a function of the energy of the incident radiation and the character of the material. It is the purpose of this research to more accurately characterize these properties with the nature of ceramic materials.

Ultra-Violet Photolysis Study

James D. Siegwarth
Senior Research Associate, Ceramic Engineering

Jack K. Merrow
Predoctoral Associate, Ceramic Engineering (December 16 to June 15)
Ph.D. Thesis Research

Lakshmi Annapoorni
Research Assistant, Ceramic Engineering (December 16 to June 15)
Ph.D. Thesis Research

The purpose of this research is the study of radiation damage to white ceramic materials. The specific interest is in ultra-violet radiation damage to MgO single crystals with the intention of applying knowledge gained with this work to the more general problem of radiation damage to thermal control coatings.

Preparation is underway to study the thermal luminescence of MgO. A spectrometer and double monochromotor have been received and a liquid nitrogen cryostat and associated vacuum system are nearing completion. The required electronic equipment has either been purchased or built. The sample temperature control system is nearly complete.

This system should be in operation by the middle of the summer. It is desired to supplement the thermoluminescence work with both electroluminescence and Electron Spin Resonance in the future. Equipment will be available for both. Hopefully, the mechanisms involved in the radiation damage will be identified by this work and some progress made toward the ultimate control or elimination of this damage.

FERROELECTRIC MATERIALS STUDY

Robert J. Cambell, Jr.
Assistant Professor, Ceramic Engineering

The objective of these studies is the development of an explanation of the mechanism of energy storage in ferroelectric materials, resulting from displacement of atoms in the crystal lattice.

Time Dependent Properties

Tracy L. Scott
Research Assistant, Ceramic Engineering (December 16 to June 15)
M.S. Thesis Research

Earlier work on barium titanate demonstrated the influence of grain size on the change of dielectric constant with time.

Studies thus far have shown that the aging rate varies inversely with grain size when the grain size was controlled by additions of iron.

A hot press has been constructed to prepare dense fine grain samples and the initial samples have been prepared. These samples have not been satisfactory to date because of radial cracking. Several unsuccessful procedural modifications have been made but the method is still being studied.

Ferroelectric Structure

Richard E. Deno (Office of Engineering Research)
Research Assistant, Ceramic Engineering
M.S. Thesis Research

The correlation of polarization with mechanical deformation of ferroelectric polycrystalline materials has reached an apparatus construction stage.

A strain cage capable of producing compressive stress while subjecting the sample to vibratory stress has been completed.

Oxidation Studies in Colored Glass

James W. Vogan (Unsupported)
Part-time Graduate Student, Ceramic Engineering
M.S. Thesis Research

A study of electrochemical potentials is expected to reveal the influence of oxidizers and firing atmospheres on the oxidation potential of iron in glass melts.

The initial system intended to employ the FeO, Fe_2O_3, SiO_2 system. The melting temperatures proved to be too high for the platinum electrode system. The melting point was reduced by changing to the Al_2O_3, SiO_2 eutectic composition. Platinum electrodes were still unsatisfactory. Molybdenum electrodes protected by an argon atmosphere are now being used.

DEFECT PROPERTIES OF IONIC AND CERAMIC CRYSTALS

Thomas G. Stoebe
Assistant Professor, Metallurgical Engineering

This investigation concerns the growth and perfection of ionic crystals and the study of their defect properties.

Growth and Perfection of Single Crystals

Hira L. Fotedar (Office of Engineering Research)
Graduate Assistant, Metallurgical Engineering
M.S. Thesis Research

Richard L. Trantow
Undergraduate Aide, Metallurgical Engineering

The purpose of this project is to develop a capability for the production of LiF and MgO single crystals with known defect structures for use in mechanical properties and optical studies. Accomplishments during this report period include preliminary crystal growth experiments using the Kyropolous technique in air, and the development of a setup which allows growth in a controlled atmosphere.

Equipment has been acquired and the experimental setup has been designed for the use of ionic conductivity measurements to monitor the defect structure of the crystals which will be produced. The literature survey has continued in the fields of mechanical properties and MgO crystal growth.

A paper entitled "Lattice Defects and Defect Interaction in Lithium Fluoride Crystals" by T. G. Stoebe was presented at the American Institute of Mining and Metallurgical Engineers meeting held in Los Angeles, California, February 1967.

SURFACE PHENOMENA

Many properties of ceramic materials are governed by the character of the grain boundaries of the polycrystalline composite. This research area was established to obtain fundamental information regarding the chemistry and physics of the surfaces of ceramic materials.

ALUMINUM OXIDE BICRYSTALS

William D. Scott
Assistant Professor, Ceramic Engineering

The purpose of this research is to study grain boundary effects in macroscopic bicrystals of aluminum oxide by controlling misorientation and environment during their preparation.

Mechanical Properties of Aluminum Oxide Bicrystals

Henry Y. B. Mar
Predoctoral Associate, Ceramic Engineering (December 16 to June 15)
Ph.D. Thesis Research

The purpose of this project is to produce aluminum oxide bicrystals with controlled misorientation and to study the mechanical properties of the grain boundaries as a function of misorientation, stress and temperature.

Pressure-sintered bicrystals are being produced in the apparatus described in earlier reports. Experiments are being carried out to determine the effect of thermal expansion mismatch on spontaneous cracking in bicrystals. A model predicting fracture arrays has been developed, and specimens for a series of misorientation experiments have been oriented, cut and polished flat. Initial experiments on specimens with thermal expansion mismatch show the expected fracture patterns.

Internal stresses from thermal expansion mismatch are not usually considered to be significant in aluminum oxide. This study should provide information on the true magnitude of internal stresses as they related to fracture initiation in alumina.

A paper entitled "Reheat Bloating of Hot Pressed Materials" by W. D. Scott was presented at the Tri-Section Meeting, American Ceramic Society, held in Yakima, Washington, May 1967.

Pore Growth and Pore Removal in Grain Boundaries of Aluminum Oxide

William D. Scott
Assistant Professor, Ceramic Engineering

The purpose of this project is to study the formation and subsequent removal of pores located on grain boundaries in aluminum oxide bicrystals, and to relate this pore behavior to sintering and diffusion in aluminum oxide.

Further annealing studies have been carried out in pores in the boundaries of new bicrystals. The development of boundary pore structures is being followed. A direct relationship between the surface roughness of the crystals used in fabrication of bicrystals has been established, and reproducable pore structures are being obtained.

Future work will attempt to relate the rate of change of pore shape to surface and grain boundary diffusion in alumina.

Interfacial Energies of Aluminum Oxide Bicrystals

James F. Shackelford
Research Assistant, Ceramic Engineering (December 16 to June 15)
M.S. Thesis Research

Steven T. Burnum
Undergraduate Aide, Ceramic Engineering

The purpose of this project is to determine the relative interfacial grain boundary energies in aluminum oxide by measuring the profile of thermally etched boundaries.

A computer curve fitting and output plot program have been developed to analyze the shape of thermally etched grooves. A series of specimens for bicrystal fabrication have been oriented, cut and polished flat. Pressed bicrystals have been fabricated and are now being thermally etched.

A simple tilt boundary with misorientation selected to produce pure edge dislocations will be investigated and results will be compared with current theories on grain boundary structures.

The Effect of MgO Impurity on Relative Interfacial Energy in Alumina

Michael Matson (Unsupported)
Part-time Graduate Student, Ceramic Engineering
M.S. Thesis Research

The purpose of this project is to measure the effect of the presence of MgO on the grain boundary energy of alumina and to correlate this effect with current theories of sintering in alumina.

Specimens of high purity alumina have been oriented, cut and polished flat. Initial thermal etching experiments are being carried out in cooperation with Mr. Shackelford. Selected tilt boundaries similar to those studied in the investigation on grain boundary structures will be fabricated, and the effects of impurities and deliberate MgO doping will be investigated.

Impurity Diffusion in MgO Under the Influence of an Electric Field

Chester A. Hinman
Predoctoral Associate, Ceramic Engineering (December 16 to June 15)
Ph.D. Thesis Research

The purpose of this project is to investigate the diffusion of nickel in MgO at high temperature and in an electric field. By using the microprobe to measure the drift of the diffusion profile in a sandwich diffusion couple, one can obtain, with the help of other bulk diffusion data, the mobility and effective change of the nickel ions. Information can also be obtained on the diffusion mechanism.

The Centorr furnace has been assembled and checked at 1500°C. Resistivity of pure and Ni doped MgO has been measured and a trial diffusion run has been carried out. Microprobe analysis techniques are now being developed.

Once the fabrication, annealing and analyses techniques are well established, high purity MgO single crystals, which are on hand, will be used for the final experiments.

SURFACE DIFFUSION

Jerry E. Turnbaugh
Assistant Professor, Ceramic Engineering

Edward H. Randklev
Research Assistant, Ceramic Engineering (March 16 to June 15)
Ph.D. Thesis Research

The purpose of the project is to measure surface diffusion coefficients in order to obtain information upon the structure and chemical nature of the surface of ceramic materials.

Construction of apparatus and survey of literature are continuing. Preliminary calculations based on literature data indicate that the system Al_2O_3-Cr_2O_3 is experimentally suitable.

PROCESSING

Research in this area is intended to gain information relative to the effect of processing variables upon the micro- and macro-structure of ceramic materials and upon their resultant properties.

CERAMIC PROCESSING

O. J. Whittemore, Jr.
Associate Professor, Ceramic Engineering

Initial Stages of Sintering

J. Joseph Sipe
Predoctoral Associate, Ceramic Engineering (December 16 to June 15)
Ph.D. Thesis Research

The objective of this project is to study the initial stages of sintering where pore growth occurs. This phenomenon has been shown to occur during the sintering of several ceramic materials although it also has been shown to occur simultaneously with shrinkage. Auxiliary objectives are to determine whether pore growth occurs generally and the controlling mechanisms.

Rate determinations were made on pore growth during the sintering of iron oxide (Mapico 297) at temperatures from 500 to 700°C. From these determinations, the activation energy of pore growth of iron oxide was calculated as about 15 K cal/mole, about one-tenth the value published for the activation energy of shrinkage.

A paper entitled "Pore Growth During Sintering of MgO, Fe_2O_3 and Al_2O_3" by O. J. Whittemore, Jr. and J. Joseph Sipe was presented at the Annual Meeting of the American Ceramic Society, New York City, May 1967.

Development of Electrical Porcelain from Pacific Northwest Materials

Donald Wadekamper (Edward Orton Jr. Ceramic Foundation Fellowship)
Research Assistant, Ceramic Engineering
M.S. Thesis Research

The objective of this project is to develop electrical porcelains utilizing ceramic raw materials from the Pacific Northwest. Properties of the raw materials will be related with the resultant properties of the porcelains.

A typical porcelain has been compounded of commercially available feldspar, flint and clay. Substitutions of Lake Wenatchee albite, Lane Mt. silica fines, and Ione kaolin will be made.

Characterization and Forming

Douglas J. Calkins
Predoctoral Associate, Ceramic Engineering (December 16 to June 15)
Ph.D. Thesis Research

Daniel Leiser
Research Assistant, Ceramic Engineering (December 16 to June 15)
M.S. Thesis Research

The objective of this project is to study ceramic forming methods and to correlate characterization of particles and agglomerates with forming and subsequent product properties. Present activities are being devoted to the study of compaction.

Compaction curves of glass spheres have an "S" shape not shown by previous investigators. This observation may indicate a larger contribution to compaction from fracture than from rearrangement because of the larger regular-sized glass spheres. Preliminary compaction curves have been conducted on through 35 on 42-mesh fused alumina and fused mullite-particles. The effect of compaction rate within the range possible with the Instron machine has shown compaction to be inversely proportional to rate.

Compaction cells have been designed for studies of particle arrangement and pore distribution after compaction.

EFFECT OF LANTHANUM DOPING UPON BARIUM TITANATE

James I. Mueller
Professor, Ceramic Engineering

Ronald P. Burley (National Lead Co. Fellowship)
Research Fellow, Ceramic Engineering
M.S. Thesis Research

This investigation was initiated to determine the effects of processing parameters such as type of lanthanum additive, firing temperature and furnace atmosphere upon the micro- and macro-properties of barium titanate.

Lanthanum doped barium titanate discs were prepared by the TAM Research Laboratory. C. P. $BaTiO_3$ was doped with lanthanum oxalate and lanthanum nitrate. Both line scans and raster displays were made with the electron microprobe. Segregation of lanthanum is found to occur in only one specimen and this is attributed to poor mixing. Segregation occurs as separate grains of higher lanthanum concentration. These grains also have a lower barium concentration but the titanium concentration is essentially constant.

Photomicrographs were taken of polished and etched specimens. Addition of lanthanum is found to inhibit grain growth with the nitrate being more effective in this respect than the oxalate. This may be due to the soluble nature of the nitrate. No barrier layers were observed at grain boundaries although oxygen distribution was not determined.

APPENDIX A-1

Distribution of Projects Within the University According to Research Areas

Academic Department	Number of Projects	Zr-O-C	Solid State	Surface	Process
Chemistry	1	1	-	-	-
Ceramic Engineering	13	3	3	5	2
Electrical Engineering	1	-	1	-	-
Metallurgical Engineering	4	3	1	-	-
Physics	1	-	1	-	-
TOTAL	20	7	6	5	2

APPENDIX A-2

Number of Students and Faculty Involved in Research Supported by Grant Funds

Academic Department	Number of Projects	Faculty	Research Faculty	Under Grads	MS	Ph.D.	Total Grads
Chemistry	1	1	-	-	-	1	1
Ceramic Engineering	13	4	2	1	3	11	14
Electrical Engineering	1	1	-	-	-	1	1
Metallurgical Engineering	4	4	-	1	2	1	3
Physics	1	3	-	-	-	1	1
TOTAL	20	13	2	2	5	15	20

APPENDIX B

Ceramic Materials Research Seminars

"Radiation Damage in Aluminum Oxide"
Dr. Terry D. Gulden, General Atomics, San Diego, California

"Research in Ceramic Processing"
Mr. O. J. Whittemore, Associate Professor of Ceramic Engineering

"Mössbauer Effect of Fe^{57} in $FeCl_2$"
Mr. Duane P. Johnson, Predoctoral Research Associate, Department of Physics

"Discussion of Rock-Salt Structure Transition Metal Oxides"
Dr. Robert G. Lye, Research Institute of Advanced Studies, Martin Company, Baltimore, Maryland

"Thermal Expansion of Anisotropic, Polycrystalline Ceramics"
Dr. Jerry E. Turnbaugh, Assistant Professor of Ceramic Engineering

"Liquid Metal Embrittlement and Brittle Fracture in Zinc"
Dr. M. H. Kamdar, Research Institute of Advanced Studies, Martin Company, Baltimore, Maryland

"Structures of Liquid Silicates from Density Measurements"
Mr. D. R. Gaskell, Research Staff, Department of Metallurgy and Metallurgical Engineering, McMaster University, Hamilton, Ontario, Canada

"Band Structure Determinations of Zirconium Carbide"
Mr. Alan D. Miller, Predoctoral Research Associate, Ceramic Engineering

"Processing of Polycrystalline Ferroelectrics"
Mr. Robert J. Campbell, Jr., Assistant Professor of Ceramic Engineering

"Structural Aspects of Zeolite 'Faujasite'"
Dr. Verner Schomaker, Professor and Chairman of the Department of Chemistry

"Diffusion and Solubility of Helium Gas in Uranium Dioxide"
Mr. Pei Sung, Predoctoral Research Associate, Ceramic Engineering

"Solid State Electro-Diffusion"
Mr. Chester A. Hinman, Predoctoral Research Associate, Ceramic Engineering

"Half a Century Plus of Research in Glass"
Mr. George McLellan, Corning Glass Works, Orange, California

"Thermoluminescence and Decay Measurements of Luminescent Materials"
Mr. Larry D. Riley, Project Leader, Electro Optical Measurements Group, Advanced Materials Department, Display Devices Development, Tektronix, Inc.

"Metal Carbide Research at the Lewis Flight Center"
Dr. H. B. Probst, Head, Refractory Compounds Section, Materials Structure Division, Lewis Flight Center, NASA, Cleveland, Ohio

"Measurements on MgO Powder"
Mr. Dean Carey, Research Engineer, Tektronix, Beaverton, Oregon

APPENDIX C

Papers Published:

"180° Domain Formation in Ferroelectrics with Shorted Electrodes," John L. Bjorkstam and Richard E. Oettel, Bulletin American Physical Society, 12, p.557 (1967).

"Debye-Waller Factor for FeF_2," D. P. Johnson and J. G. Dash, Bulletin American Physical Society, 12, p.378 (1967).

"The Effect of Plastic Deformation on the Resistivity and Hall Effect of Copper-Palladium and Gold-Palladium Alloys," M. J. Kim and W. F. Flanagan, Acta Metallurgica, 15 (1967).

"An Approximate Density of States Curve and its Relation to the Measured Electrical Resistivity of Gold-Palladium Alloys," M. J. Kim and W. F. Flanagan, Acta Metallurgica, 15 (1967).

"The Recovery Kinetics of Deformed Copper-Palladium and Gold-Palladium Alloys," M. J. Kim and W. F. Flanagan, Acta Metallurgica, 15 (1967).

"Relationship Between Dislocation Density and Flow Stress in Materials Deforming by a Peierls Mechanism," Donald J. Bailey and W. F. Flanagan, Philosophical Magazine, 15, 43 (1967).

"Mössbauer Effect of Divalent Fe^{57} in NiO and MnO," J. D. Siegwarth, Physical Review, 155, p.285 (1967).

Papers Accepted for Publication:

"180° Domain Formation in Ferroelectrics with Shorted Electrodes," J. L. Bjorkstam and Richard E. Oettel, Physical Review.

Papers Submitted for Publication:

"A Novel Clamping Technique for a Mössbauer-Cryostat," D. P. Johnson, G. A. Erickson and J. G. Dash, Review of Scientific Instruments.

"Calculation of the Temperature-Dependent Shear Modulus of UO_2," J. E. Turnbaugh and Pei Sung, Journal of Nuclear Materials.

"Calculation of Diffusivity and Solubility with Error Analysis for Diffusion in a Sphere," J. E. Turnbaugh and Pei Sung, Journal of the American Ceramic Society.

Papers Presented:

"Debye-Waller Factor for $FeCl_2$," D. P. Johnson and J. G. Dash, American Physical Society, Chicago, Illinois, March 1967.

"Reheat Bloating of Hot Pressed Materials," W. D. Scott, Tri-Section Meeting of the American Ceramic Society, Yakima, Washington, May 1967.

"Lattice Defects and Defect Interaction in Lithium Fluoride Crystals," T. G. Stoebe, Metallurgical Society, AIME, Los Angeles, California, February 1967.

"A Model for the Commencement of Serrated Yielding in BCC Iron," D. J. Bailey and W. F. Flanagan, Metallurgical Society, AIME, Los Angeles, California, February 1967.

APPENDIX D

Distribution

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