UNIVERSITY OF WASHINGTON

College of Engineering

Ceramic Engineering Division

Multidisciplinary Research Activity on the Nature and Properties of Ceramic Materials

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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, mechanical, atomic and molecular, and processing. The research program is planned and coordinated by the Ceramic Materials Research Committee, appointed by the Dean of the Graduate School. The current membership includes James I. Mueller, Ceramic Engineering, Chairman and Principal Investigator; T. F. Archbold, Metallurgical Engineering; J. Gregory Dash, Physics; Billy J. Hartz, Civil Engineering; Irene C. Peden, Electrical Engineering; and O. J. Whittemore, Jr., Ceramic Engineering. Administration of the program is coordinated by a board consisting of E. C. Lingafelter representing the Graduate School, Chairman; H. Myron Swarm, Associate Dean, College of Engineering; D. A. Pifer, Chairman of the Department of Mining, Metallurgical and Ceramic Engineering; and James I. Mueller, Principal Investigator.

GENERAL PROGRAM REPORT

This is the twelfth semiannual status report and it covers the second half of the sixth year of operation under this grant. During the report period, a total of twenty-nine projects were supervised by eighteen faculty members in eight academic disciplines of the University. Dr. David B. Fischbach joined the ceramic engineering faculty effective June 1, 1969 as a research associate professor. Dr. Fischbach will organize and supervise students on the nature and properties of carbon and graphite.

The Ceramic Materials Research Seminar, a period devoted to discussions of concepts and research of interest to the program, met for a total of three sessions during the report period. A complete list of seminar speakers and their topics is included as Appendix B.

The program supported the attendance of eight faculty members to a total of five technical meetings at which three papers based upon work supported by the grant were presented. 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.

Since the Annual Meeting of the American Ceramic Society was held in Washington, D.C., it was mutually agreed that the Spring Technical Review would be held in Washington. Professors Björkstam, Dash, Kast, Miller, Mueller, Scott and Whittemore presented a review of the Ceramic Materials Research Program to representatives from NASA Headquarters and several of the Research Centers. The response to such a review was very encouraging and similar but smaller review teams will visit various Research Centers in the future.

RESEARCH STAFF

Faculty Supervisors:

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D. J. Calkins, Ceramic Engineering
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B.S. Mechanical Engineering

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C. S. Krishnan, Ceramic Engineering
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T. W. Woller, Machinist

CHEMICAL

This system was selected as the subject for study of the effects of chemical environment upon ceramic materials. Several faculty members from various disciplines are participating in a coordinated program to obtain 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 affect 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.

Influence of Oxygen Activity on the Structure of Zirconium Oxide

K. M. Nair
Predoctoral Associate, Ceramic Engineering
Ph.D. Thesis Research

The purpose of this study is the determination of the effects of low oxygen partial pressure at high temperatures 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 oxide compounds of zirconium lower than ZrO_2 have been observed in the equilibrium study of Zr-O systems. Study has been concentrated on two typical temperatures (1) just above the monoclinic-tetragonal transformation (1200°C) and (2) below the tetragonal-cubic transformation of ZrO_2 and between $\log pO_2 = -9.8$ to $\log pO_2 = -13.5$. No observable changes both in the relative intensities and in the d-spacings are noticed, but the color of the sample varies from pure white to grey. Change of temperature in hydrogen atmosphere does not produce any change in the d-spacings. These 'black oxides' change to an almost white color when heated in air or oxygen without any change in the x-ray diffraction pattern.

Non-equilibrium study of Zr-O_o systems has resulted in a material which has a lattice parameter (a_o) of 3.8956Å with the ZnS structure. Further study on the oxidation of this material under extremely oxygen-free argon atmosphere is underway, hoping to explain the "blackening" property of ZrO_2 and the mechanism of formation of ternary compounds.

Studies of the Zirconium Dioxide-Carbon Reaction

S. K. Sarkar
Predoctoral Associate, Ceramic Engineering
Ph.D. Thesis Research

A ternary material (zirconium oxycarbide) of 98% or more purity has been produced from a mixture of ZrO_2 and carbon heated to 1800°C in a graphite-tube furnace with a CO atmosphere. The composition of this compound has not yet been established, but the lowest lattice parameter observed was 4.671Å.

Information has been obtained regarding the kinetics of oxycarbide formation at a given temperature as a function of time and CO pressures. Higher CO pressures result in the formation of oxycarbide which shows better x-ray diffraction peak resolution. Initial oxidation studies of the oxycarbide indicate that it may have a slightly better oxidation resistance than pure ZrC.

Zirconium oxycarbide has been formed from mixtures of ZrO_2 and ZrC at 1800 and 1900°C. Depending upon the temperature and CO pressure, one or two f.c.c. phases are formed. The intensity of x-ray diffraction peaks indicate the rate of oxycarbide from these mixtures is much slower than from the ZrO_2-graphite mixtures.

Compositions of zirconium oxycarbides having lattice parameters between 4.674 and 4.689Å have been determined. The relationships between the lattice parameter and the weight percents of oxygen and carbon and the mole percent carbon plus oxygen have been obtained.

At 1800°C, by the action of 'CO' pressure alone, zirconium carbide (J.P.L. a_o = 4.697Å) has been converted to zirconium oxycarbide. With decreasing 'CO' pressure in the system, the change in the lattice parameter decreases. This behavior of 'CO' pressure is opposed to the behavior of 'CO' pressure on the ZrO_2 and carbon mixture, i.e. with increasing 'CO' pressure, the lattice parameter increases. This indicates that a possible equilibrium phase is possibly being approached and investigation of this is continuing.

SOLID-SOLID EQUILIBRIUM

Norman W. Gregory
Professor, Department of Chemistry

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

Interaction of Metal Oxides with Graphite and of Metal Carbides with Metal Oxides

Juey Hong Rai
Research Assistant, Chemistry
Ph.D. Thesis Research

The objective of this research is to study kinetic and thermodynamic properties of the reaction of CaO and graphite and of ZrC and CaO by torsion effusion measurement of steady state pressures of Ca(g) and CO(g) generated in effusion cells.

Mr. Rai is in the final stages of writing his Ph.D. thesis. He expects to present his research to his supervisory committee before July 1. His thesis describes fully his method for deriving thermodynamic data from steady state effusion pressures, measured at various temperatures as a function of time. His results on the CaO-graphite reaction are in very good agreement with those predicted from complementary thermodynamic studies. A direct study of this reaction has not been reported earlier. It also appears likely that the reaction of CaO with ZrC has given results which will be useful as an aid in characterizing the ZrC phases used as initial reactants. A manuscript, possibly two, based on this work will be prepared and submitted for publication during the summer months and will be submitted as a technical report when reprints are available.

BONDING IN INTERSTITIAL COMPOUNDS

Alan D. Miller
Assistant Professor, Ceramic Engineering

A better understanding of electronic bonding in interstitial compounds is sought by this study.

Ultrasoft X-ray Emission Studies

James W. Rue
Predoctoral Associate, Ceramic Engineering
Ph.D. Thesis Research

The purpose of this project is to: (1) study the ultrasoft x-ray emission of carbon, oxygen, and zirconium in Zr-C-O compounds and (2) relate the spectral data obtained to the electronic energies in Zr-C-O compositions whose band structures have been predicted.

The primary effort during this report period was in developing techniques for preparing thin windows for the detector in the spectrometer. The problem of supporting the window against a one-atmosphere pressure differential while retaining sufficient transmission was recently solved and the spectrometer is operable. The next step is to investigate the effect of instrument error on the recorded spectra.

Structural Ordering in Zr(C,O)

John N. Hale
Research Assistant, Ceramic Engineering
M.S. Thesis Research

This project will investigate the degree of ordering, if any, in the nonmetal sublattice of Zr(C,O) phases. The behavior of these compositions in other work suggests that there may be ordering among the carbon and oxygen atoms.

Zirconium oxycarbide compositions containing up to 2.5 w/o oxygen were synthesized and their compositions determined by combustion techniques. The fabrication of one of these compositions by hot pressing in a graphite die is being studied although the density achievable to date remains low.

The powder specimens which were to be studied at Oak Ridge National Laboratory by neutron diffraction are still being characterized.

ZIRCONIUM OXIDATION

Thomas F. Archbold
Associate Professor, Metallurgical Engineering

This research project is investigating the characteristics and mechanisms of the early 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

R. Darolia
Research Assistant, Metallurgical Engineering
M. S. Thesis Research

A detailed examination of the structure, grain size, and transformation characteristics of thin zirconia films is being made by the use of electron microscopy. The kinetic data obtained by the previous student on the project, Dr. L. P. Srivastava, are being used in an attempt to predict the oxide characteristics. During the report period, Mr. Darolia has devoted his time to the preparation of oxide films and to the required training for the use of the electron microscope. In addition, a literature survey of the oxidation of ZrC is near completion.

A paper entitled "The Effect of Gas Flow Rate on the Oxidation Kinetics of Zirconium" by L. P. Srivastava and T. F. Archbold has been accepted by *Scripta Metallurgica*. Further papers are in preparation.

CALORIMETRIC INVESTIGATION OF CERAMIC AND RELATED MATERIALS

Alan D. Miller
Assistant Professor, Ceramic Engineering

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

High-Temperature Drop Calorimetry

Shiushichi Kimura
Research Associate, Ceramic Engineering

Final checkout and calibration of the calorimeter was finished during this period. The heat content of molybdenum metal was measured from 500 to 1700°K and compared with existing data. Measurements are now in progress on ZrC_{1-x} specimens, x ranging from 0.6 to $\sim$1.0.

MECHANICAL PROPERTIES

Research upon the mechanical properties of ceramic materials is underway to develop a more thorough understanding of the brittle fracture mechanisms in single crystals and polycrystalline ceramics.

ALUMINUM OXIDE BICRYSTALS

William D. Scott
Assistant Professor, Ceramic Engineering

The purpose of this work is to study the properties of grain boundaries in aluminum oxide.

Mechanical Properties of Aluminum Oxide Bicrystals

Raymond L. Bertolotti
Predoctoral Associate, Ceramic Engineering
Ph.D. Thesis Research

The purpose of this project is to study grain boundary sliding in aluminum oxide by subjecting grain boundaries of selected, controlled misorientation to pure shear loading at elevated temperatures.

Attempts to shear grain boundaries of aluminum bicrystals have apparently produced some boundary sliding. Complex combinations of basal slip and rhombohedral twinning have also been observed. Several single crystals have been deformed to obtain information on their other deformation processes so that they can be controlled during grain boundary shear. The stress and temperature dependence of twinning have been measured, and the effects of twin-slip interactions on high temperature deformation have been shown in creep experiments. Cracking at twin-twin and twin-matrix interfaces has been observed. Surface condition apparently controls twinning and this knowledge will be used to test grain boundary sliding in the absence of complicating twin-boundary interactions.

One of the primary mechanisms of polycrystalline deformation at high temperature is thought to be grain boundary sliding. The kinetics of this process and the relationship of boundary sliding to dislocation motion in the crystals adjacent to the boundary will be investigated in pressure sintered bicrystals of controlled misorientation.

Interfacial Energies of Aluminum Oxide Bicrystals

G. Achutaramayya
Predoctoral Associate, Ceramic Engineering
Ph.D. Thesis Research

The purpose of this project is to determine the relative interfacial energy of low angle dislocation tilt boundaries in aluminum oxide.

Low-angle dislocation tilt boundaries have been produced in alumina single crystals by deformation of 1550°C followed by polygonization anneal at 1800°C. The subgrains produced were very small, about 20 microns wide, with misorientation tilt of less than 1°. Experiments are in progress to try to develop larger subgrains by suitable specimen geometry and heat treatment.

Measurements of the interfacial energy of clean, low angle symmetric tilt boundaries as a function of misorientation will be used to test various theoretical models of grain boundary structures and will provide information on the actual structure of alumina grain boundaries.

ZrC COATINGS

Colin J. Sandwith
Assistant Professor, Mechanical Engineering

James D. Danberg
Research Assistant, Mechanical Engineering
M. S. Thesis Research

The purpose of this project is to determine bond strengths and microhardness and to design and apply a new test of mechanical properties of ZrC plasma flame-sprayed coatings.

Mr. Danberg has presented his thesis in final form to the graduate committee for their review and approval. Within a few weeks he will have completed the requirements for the M.S. degree and his work on the nondestructive thermal test for separation of ZrC coatings.

DEFECT PROPERTIES OF IONIC AND CERAMIC CRYSTALS

Thomas G. Stoebe
Assistant Professor, Metallurgical Engineering

This project concerns the growth of single crystals, the characterization of their defect structures, and the effects of different defect structures on the properties of materials with the NaCl structure.

Mechanical Properties of LiF Single Crystals

Hira L. Fotedar
Predoctoral Associate, Metallurgical Engineering
Ph.D. Thesis Research

David Wilson
High School Teacher Research Participant

Work on this project has concentrated on the experimental study of latent hardening, due to dislocations present on other than the slip plane, on the mechanical behavior of LiF single crystals. This has included a study of the effects of prior deformation along the compression axis and perpendicular to it.

Mechanical Properties of MgO Single Crystals

M. Srinivasan
Research Assistant, Metallurgical Engineering
M.S. Thesis Research

A study of the room temperature mechanical properties of high purity MgO and of the effects of Fe^{+3} and Ni^{+2} on these properties is nearly complete. The effects of impurity precipitation reactions are also being investigated.

Aging Behavior of LiF Crystals

J. K. Lee (NSF Trainee)
Research Assistant, Metallurgical Engineering
M.S. Thesis Research

The study of quenching and aging on the electrical conductivity of LiF has been completed. Mr. Lee received an M.S. degree in Metallurgical Engineering in June 1969. Thesis title: "Effects of Quenching and Annealing on Ionic Conductivity in Lithium Fluoride."

Crystal Growth of MgO

David Bucy
Research Assistant, Metallurgical Engineering
M.S. Thesis Research

The development of a system for plasma Veineuil growth of MgO single crystal is nearly complete and testing has commenced on the apparatus to be used in this work.

CONTINUUM STRESS ANALYSIS OF CRYSTALLINE CERAMICS

The purpose of this research is to apply modern computational methods, recently developed for complex aerospace problems to the problem of evaluation of stresses in polycrystalline ceramics caused by anisotropic material properties. This should lead to a better understanding of the mechanical properties and behavior of these materials and of the influence of crystalline structure on strength.

Stresses in Crystalline Ceramics due to Anisotropic Mismatch

B. J. Hartz
Professor, Civil Engineering

The purpose of this research is to find a better theoretical solution for thermal stresses in aluminum oxide by crystals caused by anisotropic thermal expansion coefficient mismatch, that would better correlate with experimental findings.

Due to the boundary conditions of the problem, the solution by classical elasticity does not seem possible, therefore attention is focussed on approximate numerical techniques such as "the finite element method" and closely related methods where high speed computers could be used for automatic calculation.

At present several approximate analyses have been completed using different two-dimensional finite element approximations. The results from the "plane stress" finite element program show high stresses close to the interface which generally agree with the experimental results. The results also show the warping of the crystals and an attempt is now being made to superimpose finite element plate bending solutions to take this factor into account.

Preparation is also being made to solve the problem by three-dimensional finite element analysis using the "Elas-A" program. In this connection considerable review has been made of the literature dealing with anisotropic behavior of aluminum crystals with special reference to elastic constants and co-effecients of thermal expansion.

A review has been made of a new three-dimensional technique known as the "projective method", which uses higher order polynomials and regular subdivisions to make automation of computation possible. Unfortunately the program for this analysis still has some programming "bugs" that have been difficult to find. Extensive use is expected to be made of this method as soon as the programming problems are cleared up. This method is believed capable of giving a more realistic assessment of the stresses in the bicrystals.

Grain Boundary Energy and Crystal Distortion Due to Surface Energy Changes

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

This project is aimed directly at analytical calculations of the crystal distortions and of the associated internal stress fields caused by interfused energies of aluminum oxide bicrystals. The experimental results are being obtained in the project on interfacial energies under the direction of Professor W. D. Scott.

Continum Stress Analysis of Ceramic Materials

Max D. Coon
Assistant Professor, Civil Engineering

Maurice B. Cooper
Predoctoral Associate, Civil Engineering (February 1 to June 15)
Ph.D. Thesis Research

A theoretical and experimental study of residual stresses in ceramic materials is being conducted. A favorable residual stress pattern may improve some ceramics as load carrying materials as evidenced by some pre-stressed glasses. It is well known that rapid cooling of some ceramics may introduce residual stresses. Another procedure which seems worth investigating involves making use of the ductility of ceramics at high temperatures. The thought here is to heat the material until it is ductile and then load it followed by a subsequent cooling and unloading. It is felt that this procedure may induce favorable residual stress patterns. It has been decided to conduct tests on Titanium Carbide beams. The material has been obtained and the fixtures needed for the tests have been designed. The experimental program will begin this summer.

ATOMIC AND MOLECULAR

Research in this area consists of studying the electronic properties of ceramic materials, principally metal carbides or related structures, in an attempt to gain further understanding of atomic bounding and charge transfer. Also, research on radiation effects upon ceramic materials is included.

EFFECTS OF RADIATION UPON CERAMIC MATERIALS

James I. Mueller
Professor, Ceramic Engineering

William M. Ziniker
Senior Research Associate, Ceramic Engineering

Jack K. Merrow
Predoctoral Associate, Ceramic Engineering
Ph. D. Thesis Research

Coimbatore S. Krishnan
Research Assistant, Ceramic Engineering (January 1 to June 15)
Ph.D. Thesis Research

In this study the effects of ultra violet radiation upon some ceramic materials is being investigated by the technique of thermoluminescence. A basic understanding of the thermoluminescent process in MgO in terms of lattice defects, trace impurities, and various heat treatments will be of value in the discussion of the general problem of degradation of thermal control coatings. The spectral composition of several of the glow peaks has now been measured and some of the results of other workers has been confirmed. Also, progress has been made toward measuring sample absorption at various stages of the thermoluminescence. A computer plotting program has been developed to make data taking easier. Experiments on CaO have been started in order to extend the study to similar materials. A single photon counting system is being constructed so that much weaker emissions of light can be detected. Finally, extension of the program to include the effects of crystal surface defects has been given considerable study and appears very promising as a future project.

DOMAIN DYNAMICS IN ISOMORPHOUS FERROELECTRICS

John L. Bjorkstam
Professor, Electrical Engineering

This research has been concerned with the optical and dynamical properties of domains in ferroelectric KH_2PO_4 and its isomorphs.

Ferroelectric Domains and Domain Motion in KH_2PO_4 and KD_2PO_4

Richard E. Oettel
Predoctoral Associate, Electrical Engineering (December 15 to December 31)
Ph.D. Thesis Research

Because a plateau has been reached in the experimental work, Mr. Oettel has taken a more financially rewarding position with the Boeing Company which still allows time to work on interpretation of the available experimental data and its presentation as a Ph.D. thesis. Request was made that grant funds remain available to provide for any supplies which may be necessary to conduct further experiments suggested by the ongoing interpretive work. Events have shown this to be a wise decision. We have obtained single crystals of RbD_2AsO_4. With this material we expect to gain further understanding of the abrupt decrease in domain mobility which occurs approximately at Tc-75°C in KD_2PO_4 and Tc-60° in KH_2PO_4. (Tc is the Curic temperature.) If this is due to a previously unreported phase change, the electric quadripole coupling constant of the As^{75} nucleus should reflect the change in crystal structure. We have recently performed nuclear magnetic resonance (NMR) experiments on As^{75} over the temperature range from Tc-80°C to Tc(178°K) and find no such structural change. However, the As^{75} spin lattice relaxation time seems to be strongly temperature dependent below Tc, indicating a large thermal activation energy for the As^{75} motion responsible for relaxation. Crystal plates have been prepared and a search for the mobility anomaly will be carried out on RbD_2AsO_4 within the next few days. If the anomaly is found within the temperature range covered by the NMR experiment a phase change can be ruled out and an explanation sought on the basis of a large activation energy.

We have demonstrated by plotting the logarithm of domain wall velocity vs 1/T that the 180° domain wall motion in KD_2PO_4 is a thermally activated process as expected on the basis of the Miller-Weinreich (M.W.) theory for such motion. However, the electric field dependence is not at all in agreement with M.W. theory. We attribute this to important elastic effects which depend upon the strongly temperature dependent elastic shear constant C_{66}^E.

STUDIES ON GASH

Edward C. Lingafelter
Professor, Department of Chemistry

Louis P. Torre
Research Assistant, Department of Chemistry
Ph.D. Thesis Research

The objectives of this study are to investigate the mechanism of the ferroelectricity of Guanidinium Chromium Sulfate Hexahydrate (GCrSH) and its aluminum isomorph (GASH).

A new apparatus suitable for displaying the quasi-static hysteresis loops of GASH has been assembled and is in operation. Using this apparatus, a systematic study of the effects of crystal size, voltage, and exposure to x-rays on the loops has been started.

Using this apparatus as a monitor, it has been possible to adjust a crystal to a nearly fully poled state under zero voltage and to collect a complete set of x-ray diffraction intensities for each direction of polarization. These data are currently being examined.

MÖSSBAUER STUDIES

J. G. Dash
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Edward A. Stern
Professor, Department of Physics

Robert L. Ingalls
Assistant Professor, Department of Physics

Hanan Shechter
Visiting Assistant Professor, Department of Physics

Gerald A. Erickson
Predoctoral Associate, Department of Physics
Ph.D. Thesis Research

C. D. West
Predoctoral Associate, Department of Physics
Ph.D. Thesis Research

John R. Nett
Research Assistant, Department of Physics
Ph.D. Thesis Research

Mössbauer Studies

This program is based upon the application of the Mössbauer effect to study properties of various materials with emphasis on atomic force constants, interatomic potentials, electronic valence states and distributions. The proposed program consists of three individual projects, charging in alloys, anharmonic force constants and study of insulators as a function of temperature and pressure.

The results of the charging effects in Ag-Sn alloys are enhanced by controlling the sample uniformity through careful annealing. Preliminary results on low temperature anharmonicity of Fe^{57} in UO_2 indicate results very similar to those previously reported for ThO_2. The high pressure-low temperature system has been successfully calibrated by studying the isomer shift and recoil-free fraction of Fe^{57} in copper. The system will subsequently be used to further the work on Fe^{57} in ThO_2.

A paper entitled "Fe-57 in ThO_2: Extreme Low Temperature Anharmonicity," by H. Shechter, G. A. Erickson, J. G. Dash and R. Ingalls, has been published in the Bull. Am. Phys. Soc. 14, 345 (1969).

A paper entitled "Fe-57 in ThO_2: Quadrupolar Relaxation," by R. Ingalls, H. Shechter, G. A. Erickson and J. G. Dash, has been published in the Bull. Am. Phys. Soc. 14 (1969).

A paper entitled "Comments on Divalent Fe^{57m} Quadrupolar Coupling Constants," by R. Ingalls has been submitted to the Phys. Rev.

IMPURITY DIFFUSION IN MgO UNDER THE INFLUENCE OF AN ELECTRIC FIELD

William D. Scott
Assistant Professor, Ceramic Engineering

Chester A. Hinman (on leave)
Predoctoral Associate, Ceramic Engineering
Ph.D. Thesis Research

The purpose of this project was to measure the diffusion of Ni in MgO at high temperature in an electric field. Initial experiments disclosed anomalous reduction of the nickel impurity and apparent electrolysis of the MgO under the applied fields. The project was then modified to investigate D.C. conductivity effects in MgO.

High-purity MgO single crystals have been subjected to D.C. fields at various temperatures for long periods of time. Several two-probe and four-probe measurement techniques have been used. The D.C. conductivity increases with time and temperature. The current increases with applied field at a rate greater than expected from ohmic behavior. The results of these experiments are being analyzed to identify and separate the various conductivity mechanisms.

The graduate student working on this project has been on leave for the period covered by this report, and is working on the final presentation of his dissertation.

A paper entitled "Optical and X-ray Techniques of Structural Analysis," by W. D. Scott was presented at the Tri-Sectional Regional Meeting of the American Ceramic Society in Richland, Washington, May 1969.

A paper entitled "Impurity Deposits on Alumina Crystals," by W. D. Scott was presented at the 71st Annual Meeting of the American Ceramic Society in Washington, D.C., May 1969.

A paper entitled "Relative Energies of [$1\bar{1}00$] Tilt Boundaries in Alumninum Oxide," by James F. Shackelford and William D. Scott, has been published in the J. Am. Ceramic Soc. 51 (2), 688-92 (1968).

A paper entitled "Impurity Deposits on Alumina Crystals," by William D. Scott, has been accepted for publication by the J. Am. Ceramic Soc.

PROCESSING

Research in this area is intended to gain basic information on processes used for fabricating ceramics.

CERAMIC PROCESSING

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

Characterization and Forming

Douglas J. Calkins (NSF Trainee)
Predoctoral Associate, Ceramic Engineering
Ph.D. Thesis Research

Daniel B. Leiser
Predoctoral Associate, Ceramic Engineering
Ph.D. Thesis Research

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

Work continues actively on the study of small void filling as related to brittle fracture. A quantity of glass spheres have been sorted carefully to obtain very uniform sizing and sphericity. These are being compacted in a steel die to various pressures in an "Instron" machine so a precise density-pressure curve can be obtained. After compaction, the die punches are removed and the die with compact inserted into a penetrometer so that pore size distribution by mercury porosimetry can be determined. After pore size distribution is determined the compact is removed and sizing determined. Preliminary results indicate "S" shaped density-pressure curves, indicating more than one mechanism during compaction. First fracture occurs at 15000 psi, with these well sized glass spheres.

A number of compaction curves have been determined on fused mullite, a material available in two different particle shapes. A study was made of compaction at low pressures which gave "S" shaped curves indicating two mechanisms (the two mechanisms were postulated by Cooper and Eaton as large hole filling by reorientation and small hole filling by fracture). Determination of coefficients for the Cooper and Eaton equation has not been as precise as anticipated.

Using smaller dies, compaction studies in an "Instron" machine are being conducted to 50,000 psi.

Initial Stages of Sintering

J. Joseph Sipe
Predoctoral Associate, Ceramic Engineering
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, and it has also been shown that it may occur simultaneously with shrinkage. Surface diffusion is thought to be the primary mechanism of pore growth (temperatures are too low for evaporation/condensation to be significant).

Work is underway on studies on Fe_2O_3. Previous work has determined activation energy for pore growth of this oxide. Attempts will be made to obtain independent data on diffusion coefficient and reaction rate by grain-boundary grooving. Consideration is being made of a model for pore growth by surface diffusion. The conventional two-sphere model used for sintering studies does not give information on pore size or growth.

MISCELLANEOUS

SURFACE DIFFUSION

Alan D. Miller
Assistant Professor, Ceramic Engineering

Edward H. Randklev
Predoctoral Associate, Ceramic Engineering
Ph.D. Thesis Research

The primary objective of this study is the determination of the effect of temperature on the diffusion coefficient of chromium on aluminum oxide.

The furnace and necessary fixturing for the diffusion couples is complete. The fabrication of point sources for the couples was accomplished and preliminary diffusion annuals are in progress. Electron microprobe analysis will be started in the near future.

SINTERING OF CALCIA

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

James T. Benson (Teaching Assistant)
Research Assistant, Ceramic Engineering
M.S. Thesis Research

The objective of this study is to determine the significant factors in sintering calcium oxide, using calcium hydroxide as the precursor. Comparison will be made between reagent grade calcium hydroxide and several commercial hydrated limes.

In addition, dense grog (or aggregate) of sintered calcia will be sized and recombined and processed into refractory shapes. The properties of these refractories will be determined.

Arrangements have been made to insert a test panel of calcia brick (when developed in the sintering study) in the air heating furnace at Langley which is used for reentry-type tests. The high use temperature and low cost of calcia indicate this material may be a superior refractory for such furnaces.

PORE STRUCTURE OF BONE

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

A study of the pore size distribution of rat tibia and femurs has been conducted by Professor O. J. Whittemore, Jr. and Mr. J. Joseph Sipe in cooperation with Dr. David J. Baylink of the Veterans Administration Hospital and the University Medical School. Mercury porosimetry has been shown to give more precise quantitative information on the pore sizes and their volumes in bone than other techniques such as electron microscopy.

ELECTRIC GENERATOR USING BODY HEAT

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

Alan P. Fasy
Senior, Ceramic Engineering

A proposal was made in a senior design class for an electric generator constructed from high-output thermocouples to operate on the temperature difference between the human body and cold ambient temperatures. Preliminary calculations indicate sufficient power could be generated for a radio receiver.

CERAMIC MATERIALS RESEARCH PROGRAM IMPACT STUDY

James E. Rosenzweig
Professor, Management and Organization

Fremont E. Kast
Professor, Management and Organization

John W. Stockman
Predoctoral Associate, Management and Organization
Ph.D. Thesis Research

The objective of this study is to determine the impact of the Ceramic Materials Research Program upon the University of Washington. The study will investigate the impact of the CMRP at three levels: (1) the Ceramic Engineering Division, (2) the College of Engineering, and (3) the University.

During the first phase of the study we identified the administrative, organizational, and structural relationships of the CMRP from the beginning of the program in 1963 to the present time. We investigated the changes in the program and the factors causing these changes. Various measures of the level of program activity--such as number of graduate students, number of seminars, and extent of faculty involvement--were utilized. This historical perspective of the CMRP provided the basis for the interview-questionnaire phase of the study.

The second phase of the study--the interview-questionnaire program--has been completed during the past six months. This phase involved a social psychological analysis of the attitudes, opinions, and reactions of the various information from graduate students and faculty participants in the program. This was followed by personal interviews with all faculty participants and with the administrative staff in order to investigate, in more detail, questions arising from the questionnaire responses and to develop broader information and deeper insights into the program. We have also interviewed a number of people within the NASA organization to obtain information concerning NASA-sponsored University programs. This second phase of questionnaires and interviews has been completed.

We are currently engaged in the final stage of the study--the interpretation and evaluation of data and the writing of the final report. In this stage we will present our findings concerning the impact of the CMRP and will also provide information concerning the organization and administration of the CMRP, the interface between this program and NASA, and a general evaluation of progress toward program objectives.

APPENDIX A-1

Distribution of Projects Within the University According to Research Areas

Academic Department	Number of Projects	Chemical	Mechanical	Atomic & Molecular	Process	Miscl.
Ceramic Engineering	15	5	2	2	2	4
Chemistry	2	1	-	1	-	-
Civil Engineering	2	-	2	-	-	-
Electrical Engineering	1	-	-	1	-	-
Management & Organization	1	-	-	-	-	1
Mechanical Engineering	1	-	1	-	-	-
Metallurgical Engineering	4	1	3	-	-	-
Physics	3	-	-	3	-	-
TOTAL	29	7	8	7	2	5

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
Ceramic Engineering	15	5	2	2	1	12	13
Chemistry	2	2	-	-	-	2	2
Civil Engineering	2	2	-	-	-	2	2
Electrical Engineering	1	1	-	-	-	1	1
Management & Organization	1	2	-	-	-	1	1
Mechanical Engineering	1	1	-	-	1	-	1
Metallurgical Engineering	4	2	-	1	3	1	4
Physics	3	3	-	-	-	3	3
TOTAL	29	18	2	3	5	22	27

APPENDIX B

Ceramic Materials Research Seminars

"Ceramic Research at Coors" Mr. Laurence E. Ferreira, Coors Porcelain Company, Golden, Colorado

"The Relationship of Mechanical Properties to Structure in Carbons and Graphites" Dr. David B. Fischbach, JetPropulsion Laboratory, Pasadena, California

"Some Comments on Ceramics as a Reactor Materials" Dr. Hiroshige Suzuki, Associate Professor of Ceramics, Research Laboratory of Nuclear Reactor, Tokyo Institute of Technology, Japan

APPENDIX C

Theses Published:

"Effects of Quenching and Annealing on Ionic Conductivity in Lithium Fluoride"
J. K. Lee, M.S., Metallurgical Engineering

Papers Accepted for Publication:

"The Effect of Gas Flow Rate on the Oxidation Kinetics of Zirconium," L. P. Srivastava and T. F. Archbold has been accepted by Scripta Metallurgica.

"Impurity Deposits on Alumina Crystals," William D. Scott has been accepted for publication by the Journal of the American Ceramic Society.

"Effects of Lattice Defects on Thermolumnescence in Lithium Crystals," T. G. Stoebe, G. M. Guilmet and J. K. Lee has been accepted by Proceedings-International Conference on Science and Technology of Non-Metallic Crystals.

Papers Submitted for Publication:

"Comments on Divalent Fe^{57m} Quadrupolar Coupling Constants," R. Ingalls has been submitted to the Physical Review.

PapersPublished:

"Fe-57 in ThO_2: Extreme Low Temperature Anharmonicity," H. Shechter, G. A. Erickson, J. G. Dash and R. Ingalls, Bulletin of the American Physical Society 14, 345 (1969).

"Fe-57 in ThO_2: Quadrupolar Relaxation," R. Ingalls, H. Shechter, G. A. Erickson and J. G. Dash, Bulletin of the American Physical Society 14, (1969).

"Relative Energies of [$\bar{1}$100] Tilt Boundaries in Aluminum Oxide," William D. Scott, James F. Shackelford, Journal of the American Ceramic Society 51 (2) 688-92 (1968).

Papers Presented:

"Fe-57 in ThO_2: Quadrupolar Relaxation," R. Ingalls, H. Shechter, G. A. Erickson and J. G. Dash. Presented at a meeting of the American Physical Society, Philadelphia, March 24-27, 1969.

"Fe-57 in ThO_2: Extreme Low Temperature Anharmonicity," H. Shechter, G. A. Erickson, J. G. Dash and R. Ingalls. Presented at a meeting of the American Physical Society, Philadelphia, March 24-27, 1969.

"Optical and X-ray Techniques of Structural Analysis," W. D. Scott. Presented at a meeting of the Tri-Sectional Regional Meeting of the American Ceramic Society, Washington, D. C., May, 1969.

"Impurity Deposits on Alumina Crystals," W. D. Scott. Presented at a meeting of the American Ceramic Society, 71st Annual Meeting, Washington, D. C., May, 1969.

"Effects of Lattice Defects on Thermolumnescence in Lithium Crystals," T. G. Stoebe, G. M. Guilmet and J. K. Lee. Presented at a meeting of the International Conference on Science and Technology of Non-Metallic Crystals, India, January 13-17, 1969.

APPENDIX D

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