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INTERDISCIPLINARY RESEARCH CONCERNING
THE NATURE AND PROPERTIES
OF CERAMIC MATERIALS

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UNIVERSITY OF WASHINGTON
College of Engineering
Ceramic Engineering Division

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INTRODUCTION

This, the twentieth semiannual status report, covers research efforts during the second half of the 10th year of this program supported by the National Aeronautics and Space Administration with Grant Number NGL 48-002-004 for "Interdisciplinary Research upon the Nature and Properties of Ceramic Materials." Originally funded at $300,000 per year, allocations were reduced to $253,000 for 1970-71 and to $225,000 for 1971-72, $217,000 for 1972-73 and $209,000 for 1973-74.

The general objectives of the Ceramic Materials Research Program, initiated by this grant, are to encourage interdisciplinary research on ceramic materials, to assist in the graduate educational program and to develop an enduring research capability in ceramic engineering. The research objective during the first ten years of the program has been to gain additional knowledge relative to the effects of various environments upon refractory structural ceramic materials.

These reports, in the past, have dealt principally with research supported during the appropriate period. Due to a major change in our program, we are including plans for the forthcoming year. One of the several advantages of this is that it will permit the members of our program review team to have a document which not only covers our research efforts during the report period, but also gives an insight into the program which will be active during their visit. Another innovation included in this report is the identification of Research and Technology Operating Plans (RTOP's) to which our various projects are related in terms of fundamental research deemed appropriate to our University. The RTOP Current Number, as published in the FY 1973 RTOP Summary are included parenthetically beneath the title of each project.

RESEARCH PROGRAM

We indicated in our last report that consideration was being given to the modification of our research program by including an effort on solid electrolytes. Our discussions with members of the Electrochemical-Fundamentals Section, Energy Conversion and Materials Science Division, NASA-Lewis Research Center, have resulted in a substantial interest by sufficient members of our faculty to initiate research in this area.

During the past ten years we have studied the effects of various energy environments on ceramic materials and have designated our research areas accordingly. Although the energy effects will still be of prime importance, we are revising the organization of our program into three broad research areas: REFRACTORY STRUCTURAL CERAMICS, SOLID ELECTROLYTE CERAMICS and PROCESSING. Our previous interests in energy effects and process readily can be applied to either or both of the materials areas. Much of our continuing research will be in the Refractory Structural Ceramics area and most of our new projects will be in the area of Solid Electrolyte Ceramics.

The reduced funding level and the effects of the inflationary spiral over the past four years has resulted in some obvious reductions in effort. The Research Committee has attempted to give maximum support to graduate students in the several disciplines involved in our program. This has been accomplished by (1) reducing allocations for capital equipment, (2) offering student support at only the lowest stipend level regardless of the student standing in the graduate school, (3) reducing faculty travel, (4) elimination of one visiting summer professor program, and (5) withdrawing support of projects considered to be marginal to the objectives of the program.

Table I compares the level of activity for the past four years with that planned for 1973-74. Table II shows the effect of inflation in salaries, purchases and indirect costs on a hypothetical 1963-64 research program funded at $300,000. The salaries of the several faculty members indicated, but not identified, are actual values. No specific items of equipment and supplies were identified but rather a general cost-increase value based upon local studies was applied.

Table I

Comparison of Research Activity, 1969-74

	1969-70	1970-71	1971-72	1972-73	1973-74
Funding Level	$300,000	$253,000	$225,000	$217,000	$209,000
Number of Projects	39	33	21	22	19
Number of Academic Disciplines	7	7	6	6	5
Number of Faculty Supervisors	21	17	12	12	15
Number of Research Faculty	2	1	1	1	2
Number of Post Doctoral Associates	-	-	-	1	2
Number of Graduate Students	33	38	22	22	19
(MS)	(9)	(15)	(6)	(7)	(9)
(Ph.D.)	(24)	(23)	(16)	(15)	(10)

Table II

Effect of Salary Increases and Changes in Overhead Costs
Ceramic Materials Research Program

	Level of Effort (Man-months)	1963-64	1966-67	1969-70	1973-74
Professors					
1	1	$ 1,223	$ 1,690	$ 2,224	$ 2,454
2	1	1,451	1,686	1,904	2,550
3	0.7	1,159	1,439	2,067	2,252
4	0.7	1,268	1,408	1,600	1,805
Associate Professors					
1	2.5	2,250	3,668	4,498	5,495
2	1	1,289	1,600	1,859	2,273
3	1	1,200	1,556	1,881	2,253
Assistant Professors					
1	2.5	2,250	2,835	3,650	4,720
2	2.5	2,000	2,500	3,243	4,155
3	0.7	595	721	943	1,157
4	1	912	1,067	1,249	1,532
5	2	2,024	2,556	3,094	4,746
6	1	1,023	1,323	1,695	1,838
Research Faculty	17.5	15,575	19,792	24,185	30,555
Graduate Students					
Predoctoral Associates II	80	21,312	26,720	31,600	36,960
Predoctoral Associates I	135	38,475	42,255	48,600	58,185
Research Assistants	108	28,836	31,536	36,180	43,740
Support Personnel					
Principal Investigator	5.5	9,290	10,968	12,282	15,224
Secretarial	15	5,309	5,789	8,565	11,263
Engineering Aide	12	7,164	8,550	9,824	11,298
Machinist	6	3,000	3,504	5,040	6,126
Visiting Professors	0.5	550	550	650	700
Undergraduate Student Helpers	20	4,910	7,013	7,280	8,840
Total Salaries and Wages		$153,065	$180,726	$214,113	$260,121
Employee Benefits		10,384	12,703	15,332	23,518
Supplies, Equipment, Travel, etc.		77,914	82,476	95,672	111,936
Indirect Costs		58,637	55,181	79,222	122,257
(basis)		(25% Total)	(20% Total)	(37% Sal.)	(47% Sal.)
TOTAL		$300,000	$331,086	$404,339	$517,832

RESEARCH AREAS AND PROJECT REPORTS

REFRACTORY STRUCTURAL CERAMICS

Where previously we have identified our research areas by the type of energy environment or by bulk or surface phenomena, we are, with this report, placing our research of the Refractory Structural Ceramics into one of two categories: (1) Carbon and Carbides and (2) Oxides. The process research is deemed to be of such importance as to identify this as the third research area. We will continue to have group interests in such areas as Surface Phenomena, Zr-O-C and Mechanical Properties although these will not be separately noted in this or future reports.

CARBON & CARBIDES

This grouping of research projects consolidates the previously supported carbon materials research and the bulk of the area previously described under the zirconium-oxygen-carbon system.

Mechanical Behavior of Carbon Fibers (Continuing)

(RTOP: 501-21-23; 501-22-03; 502-21-20; 502-31-52)

Faculty Supervisor:	David B. Fischbach Research Associate Professor, Ceramic Engineering
Graduate Assistant:	Roy E. Henrichsen, Ph.D. Candidate Predoctoral Research Associate
Objective:	To investigate the internal friction, the dynamic and static elastic modulus, and the fracture behavior of individual carbon fibers, and correlate these properties with structure.

Background:

Investigation of dynamic modulus and internal friction behavior at low oscillatory strain levels provides sensitive techniques which have contributed significantly to understanding of the behavior of defects and their influence on the properties of many types of solids. Relatively little research of this type has been done on carbons and graphites, but studies during the last few years on conventional, pyrolytic and glassy "bulk" carbons have indicated interesting possibilities for research on defects in carbon materials by these techniques. Although the static mechanical properties of carbon fibers have been the subject of intensive research and development, dynamic properties have received little attention to date. This may be due, at least in part, to the experimental difficulties involved. The dynamic mechanical behavior of fibers has obvious practical relevance to the design and application of high-performance composites; and the unusual structural characteristics of carbon fibers offers the possibility of obtaining new fundamental insights not only into the nature of the fibers, but of carbon materials in general. Particular areas of interest in the present study include non-linear elasticity phenomena, the nature and influence of the fibrillar substructure, and the contribution of dislocations to the mechanical behavior of individual carbon fibers. A low-level effort is also being directed toward the static flexural stress-strain characteristics. These mechanical behavior studies complement the investigations on magnetic properties and structural development which are being conducted on the same fiber types.

The torsion pendulum technique has been chosen for the dynamic studies because of its applicability to single fibers, and the basic simplicity and versatility of this type of apparatus. However, the small fiber diameter ($\leq 10\ \mu m$) is a source of many experimental difficulties including apparatus miniaturization, Mechanical Behavior of Carbon Fibers (continued)

techniques for handling individual fibers, mechanical noise, air damping, etc. A vacuum split-pendulum with electrostatic excitation and optical readout has been developed. The pendulum consists of a 2.5 cm long fiber fixed at both ends, with a small mirror mounted at the midpoint which serves as the inertial member, driving armature and passive optical transducer from which a He-Ne laser beam is reflected to a self-developing photographic-paper strip chart recorder. The upper end of the specimen fiber is hung from the beam of a modified chain-type balance to permit investigation of the effects of static tensile load on the dynamic torsional behavior. The lower end of the fiber is attached to a shaft that can be rotated to apply static torsional strain in units of 360 degrees of rotation. A photo-diode actuated counter and a hand operated stop watch are used to measure the period of oscillation. The pendulum is housed in a diffusion-pumped vacuum chamber mounted on a massive vibration-isolating base supported by automotive tire inner tubes. It has been found that the apparent fiber damping capacity decreases by nearly two orders of magnitude as the chamber pressure is reduced from one atmosphere to 10^{-3} torr, then decreases more gradually (by another factor of two) and appears to level off at pressures in the vicinity of 10^{-5} torr where measurements are made.

Progress:

A major effort has been required to identify and resolve several experimental technique problems which degrade the quality of the data and/or generate artifact effects not characteristic of the true fiber behavior. Despite fairly effective isolation of the pendulum from external "seismic" disturbances, noise (especially non-torsional oscillation modes accompanied by mode coupling) has been a persistent problem at low tensile loads. This noise decreases very significantly with increasing load, and has been reduced to acceptable levels at low loads by reducing the fiber length (from 6.5 to 2.5 cm) and by developing jigs and assembly techniques to insure symmetrical mounting of the mirror sandwich on the fiber. "Duco" type cements, which are routinely and successfully employed in static tensile testing, were used to attach the fibers in initial pendulum experiments. However, rapid zero drift at high torsional strains, irregular damping behavior as a function of tensile load, and other anomalies showed this to be inadequate. Scanning electron microscope observations and an extensive series of experiments with quartz as well as carbon fibers have been conducted to develop better attachment techniques. Quartz fibers exhibit near-ideal elastic behavior in the range of our experimental conditions and have G_0 ($\simeq$ 25 GN/m^2) comparable to and diameter ($\simeq$ 11 μm) larger than that of the most rigid carbon fibers so that glue joint effects are accentuated. Significant and complex static and dynamic relaxation effects were observed with Duco-type cements. Epoxy cements perform better but are inconvenient to use because of the curing time. Diphenylcarbazide (used for whisker testing) was found difficult to control because it wets the fibers too well. A sandwich joint between thin glass plates using a meltable crystalline organic cement (Crystal Bond®, Aremco Products, Inc.) appears to give reasonable performance and is being used currently. The slow and tedious procedures and high mortality rate involved in mounting fibers for test is a problem for which patience appears to be the only solution.

Mechanical Behavior of Carbon Fibers (continued)

Preliminary room temperature dynamic behavior data have been obtained for moderate and high Young's modulus fibers made from rayon and from PAN (Thornel-25 and-75, HT-S and HM-S) at maximum dynamic strain amplitudes of (3 + 1) x 10^{-5} and a frequency of about 1.5 Hz, and some general characteristics of carbon fiber behavior have been identified. For perfectly Hookean-elastic material the apparent torsional modulus (calculated from the oscillation frequency) is influenced by the "unwinding" torques produced by static tensile and torsional stresses. The classical mechanics analysis of these effects provides a baseline for detecting non-linear effects in the carbon fibers:

$$G_1 = G_0 + P/A \qquad \text{(tensile stress)} \qquad (1)$$

$$G_2 = G_1 + AE\theta^2/12\pi L^2 \text{(torsional stress)} \qquad (2)$$

where G_0 is the true intrinsic torsional modulus, G_1 and G_2 are the apparent moduli under tensile load P or twist angle θ respectively, A is the fiber cross sectional area, E is Young's modulus, and L is the fiber length. Quartz fibers obey these relationships within the precision of our data. For carbon fibers, no unusual effects appear to be associated with tensile loading. G_1 increases with P in approximate quantitative agreement with equa. (1) (the major uncertainty is in A, especially for the irregular cross section rayon-based Thornel fibers). Typical G_0 values, in units of GN/m^2 (1.45 x 10^5 psi) are about 3 for T-25, 10 for T-75, and 25 for both HT-S and HM-S. These preliminary results indicate a very significant difference in the behavior of the two fiber types: The torsional modulus appears to be low and roughly proportional to E for rayon-based fibers, and much higher but independent of E for PAN-based fibers! According to equa. (2), G_2 should increase slightly with increasing static torsional strain. However, for carbon fibers G_2 has been found to decrease significantly as twist angle increases (sometimes after a "yield point" at low strain levels). This behavior, which is common to both types of fiber, is largely reversible up to at least 1% surface shear strain (20-30 turns clockwise or counterclockwise). Preliminary results indicate that the G_2 decrease is approximately parabolic, and the amount increases with increasing E. It is tempting to attribute this behavior to "uncoupling" of the microfibrils within the fiber.

The damping data often have considerable scatter, but the general characteristics appear to be consistent with the modulus behavior. At low static stress levels, a logarithmic decrement value of about 1 x 10^{-3} was found for all fibers, and no amplitude dependence was observed at the low dynamic strain levels used. Static tensile loads have little effect on the damping. However, damping increases approximately parabolically with increasing static torsional strain (by a factor of 2-3 for HT-S, HM-S,and T-25 and 5-8 for T-75 after about 30 turns). For T-75, at least, the damping behavior is largely reversible on untwisting, although there is some recoverable hysteresis (primarily due to the glue joint).

Mechanical Behavior of Carbon Fibers (continued)

In the area of static testing, an adaptation of Sinclair's apparatus and techniques (J. Appl. Phys. 21 380 [1950])for loop-type (elastica) microflexural testing has been developed as an undergraduate thesis project. A recording analytical balance serves as load cell, and a micrometer screw as cross-head drive. The loop, stabilized by a few turns of twist in the fiber, is immersed in a liquid lubricant to reduce frictional drag and is observed with a filar-eyepiece microscope. This simple appartus should permit more reliable determination of flexural stress-strain non-linearity and hysteresis effects. In another senior thesis project the application of carbon fiber/epoxy composite technology to improve sail battens has been experimentally investigated.

In the period ahead we plan to obtain additional room temperature data, using the improved techniques developed to date, to confirm these preliminary results and to extend the investigation to other fiber grades. Equipment modification to permit measurements as a function of temperature is also planned.

The Magnetic Behavior and Structure of Carbon Fibers (Continuing)

(RTOP: 501-21-23; 501-22-03; 502-21-20; 502-31-52)

Faculty Supervisor:	David B. Fischbach Research Associate Professor, Ceramic Engineering
Faculty Support:	John W. Macklin Assistant Professor, Chemistry
Graduate Assistants:	George B. Mellinger, M.S. Candidate Research Assistant Robert M. Haugen, M.S. Candidate Unsupported
Objective:	To measure the diamagnetic susceptibilities of carbon fibers and similar bulk carbons, and relate them to the structure to obtain further insights into the nature and structural development of these materials.

Carbons and graphites are diamagnetic; the diamagnetism is anisotropic, and the anisotropy is structure-sensitive. Magnetic measurements can therefore be used to obtain information on both the layer plan preferred orientation texture and the structural perfection (crystallinity) of carbon materials. The properties of high-performance carbon fibers depend strongly on orientation texture and on structural perfection. Magnetic susceptibility measurements are being used here both to characterize commercially available fibers and to study the structural development which occurs as a function of thermal or thermo-mechanical treatment. These studies complement the investigations on the mechanical properties of carbon fibers and on the graphitization behavior of fluidized-bed pyrolytic carbons and other forms of carbon which are also in progress.

The susceptibility measurements are made with a Faraday-type apparatus consisting of a recording microbalance (2 μg sensitivity) from which the sample is suspended between the contoured "constant force" pole tips of an electromagnet. The magnet is mounted on an adjustable-height, rotating base to facilitate location of the sample in the constant-force zone and determination of the susceptibility anisotropy. During the present reporting period, this apparatus was moved to a new location (in a basement laboratory with good thermal stability and lower background noise) and extensively renovated and modified to improve performance. The balance, an old Ainsworth two-pan equal-arm beam type in which deflection is sensed by an LVDT, has been professionally overhauled and new beam and pan-hanger knife edges have been installed. The magnet support has been modified to make it more stable, and a reversible, variable speed motor drive has been installed so that the magnet can be rotated smoothly through an angle - 180 deg. to determine accurately the anisotropic susceptibility maxima and minima. The magnet pole gap has been increased slightly to enlarge the constant-force zone. A current regulator and a precision ammeter have been added to the magnet power supply to improve stability and reproducibility of the calibration. These modifications have now been substantially completed and the apparatus set up and aligned. A complete recalibration is nearing completion. The modified apparatus appears to function very well and is expected to provide greater measurement precision and reproducibility than was possible with the original version.

Initial magnetic and density measurements on some "graphitized" carbon/carbon composites (Carbitex 700 and 730 from Carborundum Co.) and on the carbon cloth from which they were fabricated indicate that diamagnetic susceptibility may provide a useful tool for analyzing such materials. By comparison with earlier data on commercial fiber types it was confirmed that the fiber phase was a low modulus rayon-based material. A fiber volume fraction of approximately 50% was deduced. The binder phase appeared to be fairly well graphitized, and anisotropy data indicated that the binder graphite had a pronounced orientation texture (layer planes aligned parallel to the fiber axes). Some further studies on carbon/carbon composites are planned. An extension of investigations reported previously on the influence of adsorbed gases (O_2, H_2O) and of isochronal heat treatment on the magnetic behavior of carbon fibers, as well as initiation of isothermal annealing studies of kinetic aspects of thermally-induced structural evolution in fibers is planned for the period ahead.

Presentations

"The Magnetic Behavior of Carbon Materials," D. B. Fischbach, Seminar, Materials Div., Royal Aircraft Establishment, Farnborougn, U.K., 21 June 1972.

"The Magnetic Behavior of Imperfect Graphites," D. B. Fischbach, Solid State Physics Seminar, University of Washington, 9 Feb. 1973.

"The Relationship of Structure to Properties of Carbon Materials," D. B. Fischbach, Ceramic Engineering Seminar, Joint Center for Graduate Studies, Richland, Wash., 10 April 1973.

Zero Porosity Zirconium Carbide (Continuing)

(RTOP: 502-21-20)

Faculty Supervisor: Thomas F. Archbold
Associate Professor, Metallurgical Engineering

Graduate Assistant: Ramgopal Darolia, Ph.D. Candidate
Research Assistant

Objective: The present research augments the general area goal of intensive study of the zirconium-oxygen-carbon system. Previous work under this program covered the oxidation of zirconium metal for short time periods and also the structural characteristics of thin, polycrystalline ZrO_2 films. More recently, the research has been directed toward an investigation of the high temperature mechanical properties of ZrC and boron-doped ZrC.

The purposes of the present research are to develop a zirconium carbide having exceptional compressive strength at elevated temperatures and to develop a preliminary understanding of the mechanical property-microstructure relationships. At the same time, micrographs from previous experiments involving the heating of zirconium oxide films are being examined in an effort to determine the primary separation planes. The latter information is intimately involved with zirconium-oxygen and zirconium-zirconium bonding at elevated temperatures in that the thermally generated stresses are sufficiently high to cause "un-bonding" on particular planes in the tetragonal oxide.

The work involving ZrC, while having a goal of determining high temperature mechanical properties, is also related to ceramic processing in that an arc-melting method is being used to produce nearly pore-free bulk specimens. This method, followed by a homogenization anneal in a graphite furnace, has yielded polycrystalline specimens having compressive yield strengths in excess of 100 ksi at 1200°C. In addition to the near-stoichiometric ZrC material, specimens having boron contents ranging from 0.25 to 3.0 wt% are being produced and tested.

The general types of experiments being used, with yield strengths being determined as 0.2% offset, are:

ZrC

1) Yield strength vs temperature (1000°C to 1800°C).
2) Yield strength as a function of strain rate at different temperatures.
3) Stress relaxation with initial stress, initial total strain, temperature, and strain rate as variables.
4) Strain rate change at various temperatures.
5) Strain relaxation.

Zero Porosity Zirconium Carbide (continued)

ZrC + B

1) Yield strength vs temperature for various %B (1400°C-1800°C).
2) Effect of %B on brittle-to-ductile temperature.
3) Yield strength as a function of strain rate at various temperatures.
4) Stress relaxation.

Results

1) A brittle-to-ductile transition occurs with ZrC at approximately 1300°C.
2) The yield strength of ZrC ranges from approximately 115 ksi at 1200°C to approximately 29 ksi at 1800°C.
3) At 1600°C, the addition of 3%B to ZrC increases the yield strength from 64 ksi to 93 ksi.
4) At this time, these specimens are apparently the strongest bulk materials in compression at the above temperatures. The yield strength of ZrC+3%B is approximately 125 ksi at 1400°C.
5) Serrated yielding occurs in all boron-containing specimens tested at 1800°C.
6) The boron-containing specimens contain platlets of ZrB_2 in addition to the carbide and carbide-graphite eutectic products.
7) Specimen preparation for transmission electron microscopy will require spark cutting followed by ion bombardment thinning.

Plans

1) Approximately 30 specimens remain to be prepared and tested under the various conditions outlined above; the purpose is to provide additional data point for subsequent analysis.
2) Several of the observations made to date, e.g., specimen recovery, possible strain aging effects, and serrated yielding warrant further examination.
3) It is desired to examine the dislocation structures, the dislocation-diboride interactions, and the diboride growth characteristics; the lack of suitable thinning methods at the laboratory, however, will delay this aspect of the research.
4) As an MS thesis project, an unsupported graduate student is planning to assist the research with a more detailed examination of the effect of boron on the lattice parameters of ZrC; this work is generated by some preliminary x-ray studies carried out by the Ph.D. student.

Paper

"Arc Melting and Homogenization of ZrC and ZrC + B Alloys," R. Darolia and T. F. Archbold, Accepted by Metallography, June, 1973.

Bulk Properties of Zirconium Oxycarbide (Continuing)

(RTOP: 501-21-20; 502-21-20)

Faculty Supervisor:	Alan D. Miller Assistant Professor, Ceramic Engineering
Graduate Assistant:	Donald M. Fell, M.S. Candidate Research Assistant
Objective:	The objective of this study is to survey the simple mechanical, chemical and electrical properties of zirconium oxycarbide to determine if the properties are significantly affected by oxygen content.

The effect of dissolved impurities such as oxygen and nitrogen on the properties of refractory carbide phases is not well known. In particular, when the impurity level reaches levels of a percent or more, essentially no information is available. The presence of relatively large concentrations of oxygen in zirconium carbide, for example, may affect the properties out of all proportion to the concentration of the impurities. It is to check this hypothesis that this program is being carried out.

This work relates primarily to other work done or being done in Zr-C-O systems over the past few years under the Ceramic Materials Research Program.

The first phase of the study, the construction and testing of a high-temperature, resistance-heated hot-pressing facility is nearing completion. Preliminary test runs have shown that temperatures as high as 2300°C can be achieved with reserve power still available. The limiting factor at very high temperatures is oxidation protection of the graphite element. The protective atmosphere is currently being improved.

Fabrication of bulk zirconium oxycarbide specimens will be initiated in the immediate future followed by property testing.

Publication

"Oxygen Solubility in ZrC," S. K. Sarkar, A. D. Miller, and J. I. Mueller, Journal of the American Ceramic Society, 55, [12], 628-630, (1972).

Raman Studies of Zirconium Carbide (Continuing)

Faculty Supervisor:	John W. Macklin Assistant Professor, Chemistry
Graduate Assistant:	None
Objective:	The purpose of this project is to measure the Raman spectra of ceramic materials to the end of understanding the character of their bonding.

Most of our recent efforts on Raman studies of zirconium carbide have been spent studying the theoretical and experimental aspects of vibration spectroscopy of binary face-centered cubic crystals, e.g., alkali halides. These compounds probably offer the closest, well-studied spectroscopic analogy to ZrC.

The few spectra which we have recently attempted include a low temperature measurement of ZrC using equipment at Oregon State University. These first attempts met with little success, probably due to problems of sample arrangement and alignment. We must still take low temperature measurements before any final interpretation of our data. This is clearly a priority item for investigation along with the dependence of the Raman spectrum of ZrC on the carbon content.

Theoretical Study of the Electronic Properties of Disordered Carbides (New)

Faculty Supervisor:	Edward A. Stern Professor, Physics
Graduate Assistant:	Avner Zin, Ph.D. Candidate Predoctoral Research Associate
Objective:	It is the objective of this project to calculate the electronic density of states of carbide systems with a large fraction of vacancy defects using the newly developed technique described in more detail in the next section. It is hoped that such a calculation will stimulate experimental measurements to check out the details of the calculation.

Carbides as typically fabricated have such a high density of defects that it is clear that the properties of such materials are quantitatively affected by this disorder. At present, methods for calculating the electronic properties of periodic solids are well developed. However, the calculation of the effects of disorder is presently not so well developed, yet disorder effects are very important in most cases of practical importance including carbides.

We have been developing a new method to calculate the electronic properties of disordered alloys which appears to be very promising.[1,2] So far the calculations have been applied to a model calculation of a binary disordered alloy. The model is a single band, tight binding one with the atoms randomly arranged on a simple cubic lattice. Shielding is treated in an idealized way, but perfect screening is maintained. The method has been developed to the point where it would be profitable to try to calculate a real system and compare with experiments.

The method of calculation is a differential one. Consider a binary disordered alloy and imagine that at a given site one type of atom is replaced by the other type. This change will produce a change in scattering of electrons in the vicinity of this site. It has been shown[1] that this change in scattering is proportional to the change in coherent potential with concentration. The coherent potential is a periodic potential chosen such that a solid with such a periodic potential has the same density of states as the disordered solid to solving a periodic solid problem. Thus the coherent potential in essence reduces the disordered solid to solving a periodic solid problem. The method calculates the change in scattering as one constituent atom is replaced by another at a given site for an alloy of variable concentration. This determines the derivative of the coherent potential with concentration as a function of concentration. By numerical integration the coherent potential is determined and then by standard techniques the density of states of the disordered system is calculated from the known coherent potential.

<u>Theoretical Study of the Electronic Properties of Disordered Carbides</u> (cont.)

I have had a discussion with Professor Alan Miller to assess his interest in cooperating in such a research program. He has expressed interest. It is hoped, as mentioned previously, that the theoretical calculations will stimulate experimental efforts to check predictions of the theory.

References:

1. E. A. Stern, Phys. Rev. 37, May 15, 1973 (to be published).
2. A. Zin and E. A. Stern, Bull. Amer. Phys. Soc. 18, 333 (1973).

PROCESSING

A complete understanding of the nature and properties of ceramic materials is dependent upon sufficient knowledge of the effects of processing upon these properties. This area of the program is involved with a basic study of various processing techniques used in the preparation and fabrication of ceramic materials for ultimate use.

Ceramic Processing - Sintering (Continuing)

(RTOP: 501-21-26)

Faculty Supervisor:	O. J. Whittemore, Jr. Professor, Ceramic Engineering
Graduate Assistants:	Kunio Aihara, Ph.D. Candidate Research Assistant
	Harold Joss, M.S. Candidate Research Assistant
	Chattar Kucheria Research Assistant
Objective:	To study the initial stage of sintering magnesia.

In the nineteenth semiannual status report, the sintering behavior of magnesia was reported as much different in water vapor than in air and carbon dioxide. Pore growth and shrinkage rates were much greater in water vapor than in air or carbon dioxide.

The activation energy for densification in water vapor was determined to be 13 k.cal./mole, employing the equation:

$$\frac{p}{p_a} = K \ln t + C$$

where p = density, p_a = theoretical density, K = rate constant = $K_o \exp(-Q/RT)$, K_o = constant, Q = activation energy, t = time, C = constant.
This value agrees closely with the value of 15 k.cal./mole determined for the activation energy for pore growth in water vapor, as reported previously.

Activation energies for densification in air and in carbon dioxide were similarly determined, with a value of 30 k.cal./mole for both. The sintering behavior with regard to densification thus appears to be the same in these two gases.

Studies by electron microscopy have been started on the morphology of the sintered magnesia specimens. The magnesia particles are essentially of the cube (hexahedron) shape, but those in samples sintered in water vapor or at higher temperatures show somewhat less adherence to the cube shape in that other faces seem to be present, possibly octahedral or dodecahedral. The grain size noted is between 2 to 3 times the pore size obtained by mercury porosimetry. This agrees with the "pore window" in simple cubic packing - 2.3.

Ceramic Processing - Sintering (continued)

Future studies of magnesia will continue on electron microscopic observations of particle morphology and neck growth, from which correlations with mercury porosimetry and densification will be made so the sintering process can be more fully described. We will also cooperate with Professor Halsey of Chemistry and Professors Dash and Vilches of the Physics Department. We hope that these works will create new approaches to the study of sintering.

Inasmuch as sintering is a most important stage in the processing of ceramics, this work can lead to better understanding of sintering, prediction of sintering methods for control of properties, and improved properties of ceramics. Previous work in this program has indicated an optimum fine starting particle size may exist for some materials rather than the finest size as indicated by other work for the development of optimum properties, e.g., minimum grain size and maximum strength.

We further are planning to extend the research of ceramic fibers for reusable surface insulation by applying sintering studies to these materials.

Publications/Accepted for Publication

"Sintering of Silica Fiber Compacts," T. J. Ormiston and O. J. Whittemore, Jr., American Society Bulletin 52, 3, 247 (1973).

"Pore Changes in Reheating of Plasma-Sprayed Zircon," O. J. Whittemore, Jr. and D. A. Sullivan, Journal of American Ceramic Society (to be in June 1973 Issue).

"Powder Compaction in Systems of Bimodel Distribution," A. K. Chattopadhyay and O. J. Whittemore, Jr., American Ceramic Society Bulletin (to be in July 1973 issue).

"Pore Growth During the Initial Stages of Sintering," O. J. Whittemore, Jr. and J. J. Sipe (submitted for a special issue of Powder Technology).

"The Initial Stages of Sintering Hematite," J. J. Sipe and O. J. Whittemore, Jr. (in process of revision for resubmission to Journal of American Ceramic Society; original copy found acceptable with revision).

Surface Properties and Sintering of MgO (New)

Faculty Supervisor: J. G. Dash
Professor, Physics

Graduate Assistant: Toaming T. Chung, Ph.D. Candidate
Research Assistant

Objective: An experimental study of certain aspects of sintering of MgO powders, with particular emphasis on very early stages of sintering.

Vapor pressures and heat capacities of adsorbed monolayer films of He^4 and other gases are extremely sensitive gauges of the microscopic structure and homogeneity of the adsorption substrate. Since sintering of MgO cubes must involve the formation of other than (100) faces, adsorption can be applied to detect sintering at much earlier stages than possible by conventional means. It is also possible that such measurements will be able to detect the variety and quantity of other crystal planes created during the sintering process. Calorimetric and vapor pressure techniques will be similar to those currently used for studies of graphite substrates in the Low Temperature Physics Laboratory, but it is realized that certain modifications may be required for this new material.

Adsorption on Porous Solids (New)

Faculty Supervisor:	George D. Halsey Professor, Chemistry
Graduate Assistant:	David C. Hinman, Ph.D. Candidate Research Associate
Objective:	To extend earlier work on the interaction of rare gases with plane surfaces (essentially confined to carbon as graphite) to a study of higher surface area porous solids such as porous glass of the type used by Flood to investigate dimensional changes caused by adsorption.

The current status of the research is near completion of a precision volumetric adsorption appartus for use in the 80-300K temperature range, and the pressure range of 1 - 800 torr. The actual construction of the apparatus is finished, and preliminary tests are under way in the form of measurement of room temperature second virial coefficients for argon and helium. Present indications from these relatively stringent tests are that a quite high degree of accuracy may be expected.

It is believed that sufficient accuracy will be obtained to be able to verify the applicability of the two-dimensional virial expansion method of analyzing adsorption data to porous systems. The measurements consist of isotherm determinations which are fitted to give second and higher coefficients in a power series in p/kT.

The first application of our apparatus will be to the intriguing problem of pore geometry. The two-dimensional second virial coefficient of a gas, B_{2S}, is influenced by the geometry of the surface; specifically, it varies with the pore radius, and does this differently for different pore shapes. In a recent paper (J. Coll. Interface Sci. 41, 168 [1972]), Steele presents a model calculation of B_{2S} for spherical and cylindrical pores as a function of temperature and radius. It is expected that our apparatus will be able to measure departures from planar values of B_{2S} of the size calculated by Steele, and thus discern whether or not the theory is applicable to the non-planar case. A series of measurements will be attempted on porous glass well-characterized with respect to pore size distribution, with changes in pore size effected by preadsorption of a less volatile species. Similar experiments will be performed on truly microporous materials (pores of the size of a few atomic diameters) such as zeolites, in order to determine the further effect of B_{2S} of the high degree of heterogeneity expected in these adsorbents.

The Kinetics and Mechanism of Graphitization (Continuing)

Faculty Supervisor: David B. Fischbach
Research Associate Professor, Ceramic Engineering

Graduate Assistant: Ronald L. Beatty, Ph.D. Candidate
(Union Carbide Predoctoral Fellow, now at Oak Ridge National Laboratory)

Objective: To investigate the influence of initial microstructure on the graphitization behavior of disordered carbons with a wide range of structures.

Graphitization, the thermally induced evolution of metastable carbon structures toward that of hexagonal graphite, is a complex process of considerable fundamental and practical importance. It influences both the properties and the thermal stability of carbon materials. Although it is well established that graphitization is a thermally activated process and that graphitizability is a function of the microstructure, there has been little systematic study of the influence of initial microstructure (especially of hard to graphitize carbons) on the kinetic behavior. This research was undertaken to investigate, over a broad treatment temperature range, the graphitization kinetic behavior of a family of carbons with a range of structures and graphitizabilities.

Twelve pyrolytic carbons deposited in fluidized beds from a broad range of methane or propylene concentrations at temperatures of 1150 - 1900°C were isothermally annealed for periods up to 8 hours at temperatures ranging from 1350 - 3000°C. Structural evolution as a function of annealing time and temperature was monitored by room temperature measurements of the mean diamagnetic susceptibility $\bar{\chi}$ and the immersion density ρ. These data were analyzed by a curve superposition (temperature-compensated time master plot) method, which requires no detailed assumptions about analytical form of the curves, value of the pre-exponential factor, etc., to determine general characteristics and effective activation energy values ΔH for the graphitization process. X-ray diffraction measurements of mean interlayer spacing, apparent layer plane diameter and layer plane preferred orientation texture, supplemented by microstructural observations and analyses of hydrogen content, are also being employed in interpretation of the graphitization behavior.

As expected, the carbons were found to span a broad range of graphitizabilities, primarily as a function of deposition temperature. The nature and concentration of the hydrocarbon source gas were of less importance (except for the 1900°C deposits). In general, the effective activation energies increase with increasing annealing temperature, and the ΔH values cluster in three regions, indicating three kinetic regimes as a function of temperature: 175 ± 15 kcal/mole below about 1950°C; 240 ± 35 kcal/mole in the range 1950-2700°C; and 330 ± 20 kcal/mole above 2700°C. The low and intermediate ΔH values are common to most of the carbons studied but the high ΔH regime appears to be peculiar to the poorly graphitizable carbons. Kinetic analysis of the $\bar{\chi}$ and ρ data yielded generally similar results with the exception of the lowest deposition-temperature carbons where anomalies correlate with the evolution of hydrogen at low annealing temperatures and the appearance of voids at higher temperatures. The principal results of this investigation have been published in the form of extended abstracts of papers presented at carbon conferences during the last twelve months. Analysis and interpretation of the data is continuing. In the coming year it is planned to extend these studies to other poorly graphitizable forms of carbon such as glassy and fiber carbons.

Papers Presented

"Graphitization Kinetics of Fluidized-Bed Pyrolytic Carbons," R. L. Beatty and D. B. Fischbach, paper # CG-5, 11th Biennial Conference on Carbon, Gatlinburg, Tenn. 4-8 June 1973.

"The Graphitization Process," D. B. Fischbach, Lecture/Seminar, presented at the Second Industrial Carbon Science and Technology Course, Department of Metallurgy, University College, Swansea, Wales, U.K., 19 June 1972.

"Graphitization Studies on Fluidized-Bed Pyrolytic Carbons," R. L. Beatty and D. B. Fischbach, paper # P 17, Carbon '72 Conference, Baden Baden, W. Germany, 26-30 June 1972.

Publications

"Graphitization Studies on Fluidized-Bed Pyrolytic Carbons," R. L. Beatty and D. B. Fischbach, Preprints -- Carbon '72 (Deutsche Keramische Gesellschaft, June 1972) pp. 127-9.

"Graphitization Kinetics of Fluidized-Bed Pyrolytic Carbons," R. L. Beatty and D. B. Fischbach, Extended Abstracts and Program, CONF 730601 (National Technical Information Service, May 1973) pp. 30-1.

Single Crystal Growth (Continuing)

Faculty Supervisor: John H. Jones
Assistant Professor, Metallurgical Engineering

Graduate Assistant: L. A. Logan, M.S. Candidate
Research Assistant

Objective: This project includes the development of a capability for growing single crystals for use in the Ceramic Materials Research Program.

Apparatus modification for growth of Al_2O_3 and β-alumina single crystals is continuing. A flux concentrator and gas-purifying system have been constructed and the overall apparatus is nearly completed. Synthesis of these crystals in our laboratory would be of value in parts of the overall program involving mechanical and optical properties of Al_2O_3 and electrical properties of β-alumina.

OXIDES

As in the previous grouping, we have consolidated all oxide-type research that was previously identified in other research areas. As noted, several of these projects have been or will be terminated within the next few months.

Kinetics of Twinning in Aluminum Oxide (Continuing)

(RTOP: 501-01-06; 502-01-01)

Faculty Supervisor:	William D. Scott Associate Professor, Ceramic Engineering
Graduate Assistant:	Keuno Auh, Ph.D. Candidate Research Assistant
Objective:	The purpose of this work is to define the conditions of stress, temperature and surface characteristics which influence the formation and growth of deformation twins in aluminum oxide.

The kinetics of twin growth will be studied in single crystal alumina. We have observed that twin nucleation occurs from surface damage. We intend to control twin nucleation by producing mechanically or chemically polished surfaces and to introduce twins from microhardness indentations. The growth of these twins will be observed as a function of stress and temperature with attempts to extend the measurements to as low a temperature as possible towards room temperature.

During the past six months, the relevant literature on twinning in hexagonal metals has been reviewed. Single crystal specimens 1/8" diameter by 1/2" long with axial c-axis orientation have been obtained. A jig for surface polishing of these specimens has been developed to fit a new diamond polishing machine, and the first crystal has been polished.

During the next six months initial compressive tests of surface prepared specimens will be carried out. At the end of this period we should be in a position to produce controlled twin nucleation.

Significance:

The strength of aluminum oxide is governed by the initiation and propagation of cracks. There is evidence that crack initiation is common when deformation twins intersect and probably also occurs at twin grain boundary intersections. The observed effects of surface condition and temperature on the strength of aluminum oxide may be an indirect result of the effect of surfaces and temperature on twinning.

Defect Properties of Ionic & Ceramic Crystals (Continuing)

Faculty Supervisor:	Thomas G. Stoebe Associate Professor, Metallurgical Engineering
Graduate Assistant:	H. Vora, Ph.D. Candidate Research Assistant
Objective:	This project concerns the investigation of defect controlled properties of single crystals of certain ionic and ceramic materials. Included are studies of crystal growth, defect characterization, and studies of the electrical, mechanical and optical properties of such solids.

The portion of this project dealing with the effect of impurities on the thermoluminescent behavior of LiF is nearly completed. Czochralski grown single crystals of LiF have been doped with varying amounts of Ti and Mg ions and have been subjected to vacuum and HF acid treatments for removal of anions (predominantly OH). The thermoluminescent behavior of these crystals has been studied, and defects have been characterized by optical absorption and ionic conductivity techniques.

The work on LiF will help to clarify the roles of impurities and other defects which have been shown to greatly affect the thermoluminescent process.

Thermoluminescence of Pure and Doped Sapphire (Terminated)

Faculty Supervisor:	James I. Mueller Professor, Ceramic Engineering
Graduate Assistant:	John M. Rusin, Ph.D. Candidate Predoctoral Research Associate
Objective:	The object of this study was to use the technique of thermoluminescence to characterize the "as received" defect structure of pure and doped sapphire samples. Thermoluminescence was chosen because it is a very sensitive techni

Thermoluminescence in pure and doped aluminum oxide single crystals excited by X-irradiation was investigated. The resultant glow curves were highly dependent upon the manufacturing process. Because of the high common impurity level in pure and doped sapphire, positive identification of thermoluminescence defects could not be made by TL alone.

Five basic glow peaks were observed for X-irradiated pure sapphire: (1) 110°C, (2) 143°C, (3) 171°C, (4) 226°C, and (5) 280°C. The results of this study suggest that peaks 2 and 3 are associated with complexes or aggregates formed during the growth process which disassociate with subsequent heat treatment and do not reform. Peaks 1 and 4 are intrinsic defects which may be present in the "as grown" crystal or are produced upon thermal annealing.

The effect of heat treatment on the doped specimens was dependent upon the impurity content and atmosphere. Peak 5 is associated with Cr. Chromium probably is both a trap and a recombination center. The TL intensity of the peak at 123°C increased with Ti^{4+} concentration.

Peaks 1, 2, 3 and 4 had blue, red, or a mixture of blue and red for emission spectra. Peak 5 only had red emission at 550 nm. It is highly possible that there are other sources than chromium for the red emission.

The TL response to UV irradiation of sapphire was dependent upon filled deep traps or ionization of defect centers. The TL peak at 152°C was highly sensitive to UV irradiation and may involve a localized transition.

Degree

John M. Rusin, Ph.D., Ceramic Engineering, June 1973, "Thermoluminescence of Pure and Doped Sapphire."

Ultra-Violet Photolysis (Terminating)

(RTOP: 501-21-23; 502-21-27; 909-51-02)

Faculty Supervisor:	James I. Mueller Professor, Ceramic Engineering
Graduate Assistant:	Coimbatore S. Krishnan, Ph.D. Candidate Predoctoral Associate
Objective:	The purpose of this project is to utilize ESR luminescence techniques to study defect centers and their interactions due to the UV-irradiation.

Extensive data has been obtained on MgO single crystal samples to correlate thermoluminescence and trap and recombination center population decay as determined by in-situ ESR-optical techniques. Trap population decay at constant temperature has also been done to correlate with luminescence decay studies. Both the V_1 and Fe^{3+} centers have been found to take part in the charge transfer recombination luminous process. The Werz process $V_1 + Cr^{2+} \longrightarrow Cr^{3+} + V + h\nu$ has also been confirmed to occur in one sample. The data is now being analyzed for a quantitative correlation of ESR and luminescence studies.

Emission spectra have been observed for all samples. Besides the well-known R & N lines of Cr^{3+}, two sharp lines at 655 nm and 675 nm have been found at LN_2 temperatures. These are tentatively assigned to Fe^{3+} in octahedral and tetrahedral sites. The emission lines are interpreted as due to the $^4T_1\,(^4G) \longrightarrow {}^6A_1\,(^4G)$ transition of the d^5 configuration according to Tanabe-Sugano diagrams. A good fit for both the emission and absorption spectra has been obtained using the Racah parameters

$$B = 644\ \text{cm}^{-1}\ ;\ C = 2960\ \text{cm}^{-1}$$

$$D_q = 8000\ \text{cm}^{-1}\ \text{for}\ \gamma = 4.59$$

These are the same as those of Pott and McNicol for Fe^{3+} emission in tetrahedral coordination in Li aluminate. It is thought that random strains around the Fe^{3+} ion alter the strictly octahedral coordination and relax the Laporte selection rules sufficiently to allow the transitions. This also accounts for the width of the zero phonon lines and corroborates the in-situ ESR optical measurements. Complete details of the entire investigation will soon be available in thesis form.

Surface Diffusion Studies (Terminating)

Faculty Supervisor:	Alan D. Miller Assistant Professor, Ceramic Engineering
Graduate Assistant:	Edward H. Randklev, Ph.D. Candidate
Objective:	This study is concerned with the investigation of surface diffusion and the phenomenon of linear thermal facet development on surfaces of single crystal aluminum oxide (Al_2O_3). The behavior of the system with respect to these phenomena versus the variables of time, temperature, atmosphere and impurities will provide information regarding the anisotropy of surface energy and relative transport rates on the surfaces involved.

The general area of surface properties of materials is of extreme interest to the scientific community in that the techniques to study such phenomena have only recently become available. The availability of both experimental data and more realistic models of surface phenomena will permit more effective application of all classes of materials. More specifically, this study will contribute to the body of knowledge of surface phenomena in high temperature structural materials. It is closely related to programs being conducted under the Ceramic Materials Research grant on interfacial energies and deformation phenomena in aluminum oxide.

The project is still in the final publication phase. Mr. Randklev has chosen to invest a longer period of time in analysis of the data in order to insure that every conclusion possible can be drawn from the work. He has done this even though he is no longer supported by the program.

Mechanical Bicrystals (Terminated)

Faculty Supervisor:	William D. Scott Associate Professor, Ceramic Engineering
Graduate Assistant:	G. Achutaramayya Research Associate, Ceramic Engineering
Objective:	The purpose of this work is to make a critical comparison of fracture surface energy determinations by using the continuum elastic solutions (as published) with those obtained using finite-element stress analysis.

The double cantilever technique combined with the continuum elastic solutions has been used by several investigators to determine the fracture surface energies of brittle materials. The surface energy equation derived by this method is applicable for crack lengths greater than 1.5 times the crack height. For shorter crack lengths this method predicts erroneously high values of the fracture surface energy.

This work also utilizes the double cantilever technique. However, the surface energies were estimated by a finite-element stress analysis computer program provided by Professor Hartz. Experimental data on soda-lime glass was provided by Dr. S. M. Wiederhorn of the National Bureau of Standards. The finite-element method was found to predict surface energies in a fair agreement with those by the other method for longer crack lengths.

Significance:

The finite-element method showed that the calculated fracture surface energy is strongly dependent on the loading position for short crack lengths. This method also shows that the strain energy present in the material behind the loading position is very significant; a factor neglected in the other method. The applicability of finite-element method for fracture surface energy measurements was demonstrated and it was found to be better than the generally used equations at shorter crack lengths.

During this period, an attempt was also made to measure relative interfacial energies of pure and boron doped silicon carbide. Such measurements hopefully would have provided an understanding of hot pressing characteristics of pure and doped material. On annealing the specimens in argon atmosphere, the initially polished surfaces were found to facet extensively, the thermal grooves along grain boundaries could not be detected, and measurements of groove angles were not possible.

This work has now been terminated and the results of stress analyses are being prepared for publication.

Presentation

"Polygonized Boundaries in Alumina: Formation Kinetics and Interfacial Energies," G. Achutaramayya and W. D. Scott, 75th Annual Meeting of the American Ceramic Society, Cincinnati, Ohio, May 2, 1973.

Mechanical Bicrystals (continued)

Publication

"Measurement of Dihedral Angles by Scanning Electron Microscopy," G. Achutaramayya and W. D. Scott, Journal of the American Ceramic Society, Vol. 56, No. 4, April 73, pp. 230-231.

Continuum Stress Analysis of Ceramic Materials (Terminated)

Faculty Supervisor:	B. J. Hartz Professor, Civil Engineering
Graduate Assistant:	Michael Held, M.S. Candidate Research Assistant
Objective:	The application of the finite-element method of stress analysis to the results of current experimental work in the Ceramic Materials Program. The current effort is aimed at finite-element analysis of surface energy phenomena and correlation with free-surface and interfacial surface energy measurements on aluminum oxide bicrystals.

The results of calculations by Dr. Achutaramayya, referred to under "Mechanical Bicrystals," are comparable to previously published results, but were found to be sensitive to details of the test specimen and loading device which were not included in the published results. Further comparisons are to be made with test details furnished by NBS researchers.

Mr. Held is continuing efforts to match experimental surface energy results for alumina bicrystals with finite element calculations. A major source of difficulty in previous calculations was found in that the surface bar element stresses in the representation used were functions of the deformations. The actual surface tension values do not change with elastic deformation and modifications in the calculation procedure to correct the discrepancy are being made.

Support of this work has been terminated but the project is continuing and should be completed this summer.

Strain Energy in Crack Propagation (Terminated)

Faculty Supervisor: Robert J. Campbell
Assistant Professor, Ceramic Engineering

Graduate Assistant: Stephen VonTalge, M.S. Candidate
Research Assistant

Objective: An attempt is being made to correlate energy involved in propagation of cracks through polycrystalline bodies. $BaTiO_3$ bodies were chosen for models because previous work had suggested limited plastic behavior.

This project was originally intended to examine the strain energy requirements for propagation of a crack in single crystals. The intent was to employ a single crystal of $BaTiO_3$ with two areas of polarization established to provide a calibrated strain input. The amount of strain would be related to the electrical field applied. The research was stimulated by knowledge of failure of polycrystalline underwater transducers operating at high power levels. It is anticipated that this research may permit improved design of such equipment.

Difficulties in obtaining adequate single crystals have shifted the current work to a study of the energies in breaking polycrystalline $BaTiO_3$. Earlier work in this area had suggested non-elastic behavior at low stress levels. On a strain machine, stress relaxation was observed when the rate of strain application was reduced to zero.

The non-elastic behavior was confirmed in dead-weight four-point bending tests. The strain record was provided by a Datronic LVDT sensing and recording system. The strain record showed three zones. An immediate strain occurred when the load was applied. This was followed by a time dependent strain increase. The first part of this changing rate appeared to follow a parabolic pattern followed by a shift to an exponential reduction in the strain rate. Strain continued to increase for periods in excess of 24 hours.

This time-dependent strain behavior suggested creep. However, at 11.9×10^6 N/M^2 stress, strain recovery on load removal was almost a mirror image of that obtained on loading. Thus we have observed time-dependent elastic behavior.

Non-elastic strain behavior was observed at 14.2×10^6 N/M^2 stress. Residual deformation or strain of 0.065% was observed after unloading. This residual strain, as a result of loading, established a minimum yield stress in the range of 11.9 to 14.2×10^6 N/M^2. Time limitations have prevented more exact determination of the minimum yield stress.

Strain Energy in Crack Propagation (continued)

The time-dependent elastic strain has been related to domain rotation in unpolarized $BaTiO_3$ by observing the change of dielectric constant under stress. Calculations of physical changes indicate about 12 percent of the rotatable domains had rotated to provide the change of capacitance and strain.

No explanation for the residual strain on stress removal has yet been attained.

This work, by demonstrating and explaining time-dependent elastic behavior, answers some questions previously raised about this phenomenon. The demonstration of yield effects may lead to better understanding of crack propagation when the yield mechanism is revealed. This information could lead to better design criteria for high power transducers.

Degree

Stephen VonTalge, M.S. Ceramic Engineering, June 1973, "Analastic Behavior in Barium Titanate."

Gas-Solid Equilibrium (New)

Faculty Supervisor: James I. Mueller
Professor, Ceramic Engineering

Graduate Assistant:

Objective: The purpose of this research is to further study a previously identified but confused place of ZrO.

Research performed by K. M. Nair on the "unfamiliar oxidation state of zirconium and the effect of oxygen activity on the structure of ZrO_2" indicated the possible presence of a condensed phase which he suggested to be ZrO. His analysis of this material indicated it had a zinc blend-type structure with a_0 = 3.8956A. This was formed by heating powdered zirconium metal to between 760°C for 7 hours and 820° for 5 hours. The furnace was operated with argon at 1 atmosphere pressure and an oxygen pressure of 2×10^{-6} atmosphere. Although he was able to obtain this proposed condensed phase twice, further attempts were unsuccessful.

The x-ray diffraction data of this suggested phase indicated the presence of a material other than zirconium metal of ZrO_2 and is obviously a metastable phase, if real. ZrO has been reported as a gaseous specie and Nair's observation is the first indicating the possibility of a condensed phase of this composition. His evidence, although not fully substantiated, is believed to be sufficient to justify further studies.

Mössbauer Studies (Terminating)

Faculty Supervisor:	Robert L. Ingalls Associate Professor, Physics
Graduate Assistant:	C. David West, Ph.D. Candidate Predoctoral Associate, Physics
Objective:	Investigation of microscopic properties of solids such as atomic force constants, phase transitions, hyperfine magnetic and electric fields, atomic bonding.

Significance:

Provides a physical picture of the nature of solids, and ceramics in particular.

Mössbauer effect measurements are being made of hyperfine electric intensity anomalies and associated force constant anomalies in ferrous fluosilicate. Early results gave indications of anisotropic motion of the ferrous ion in the fluosilicate. It was anticipated same methods could apply to ceramic materials. Recent attempts to study such affects using a scattering technique have consumed considerable time but now appear to be successful.

SOLID ELECTROLYTE CERAMICS

(RTOP: 502-0J-51; 502-25-53)

A wide variety of possible research subjects were available for study in this area. Discussions among interested faculty, and with personnel from NASA-Lewis Research Center, suggested the most appropriate efforts on this subject would be to study the mechanisms of ionic conduction in ceramic electrolytes. Towards this end, the following research has been initiated effective June 1, 1973.

In addition to the projects listed below, the program will include work directed and performed by Dr. Suren Sarian who will join the faculty August 1, 1973 as a Research Associate Professor of Ceramic Engineering. Dr. Sarian's recognized expertise in diffusion should add considerably to our research in the solid electrolyte area.

Mechanical Relaxation (New)

Faculty Supervisor:	Leon J. Slutsky Professor, Chemistry
Faculty Support:	Leslie L. Isaacs Research Associate
Objective:	The primary objective of our effort will be to determine the jump time, activation energy, and energy of formation of the change-carrying α effect as a function of composition in materials and at temperatures where the mobility is high and to assess the utility of mechanical relaxation spectroscopy as a method of determining the parameters which govern carrier mobility.

Mechanical relaxation due to the stress-induced migration of impurities, vacancies, and interstitials has provided values of the rates, and activation energies of impurity motion and the equilibrium concentration of diffusible species in a variety of metallurgical problems: N and C in iron[1] and Cu (or Zn) in β-brass[2] being classical cases. The relaxation techniques are in general best suited to materials with relatively high mobilities where classical methods are difficult.

We have been interested in the rates of rotational ordering in ionic crystals[3] and in the rates of diffusion controlled proton transfer[4] and are presently equipped to measure velocity and attenuation of acoustic waves between 100 KC and a few 100MHz up to about 600°C. Our techniques are complementary to Professor John L. Bjorkstam's NMR measurement being suitable for very fast processes. The alkali metal and silver substituted beta-aluminas, interstitial ionic conductors with high mobility, are logical first candidates for these studies, but we would be able to collaborate with other members of the program on materials of interest to them if suitable samples can be fabricated (prisms or right circular cylinders, a few cc's volume).

In order to observe acoustic attenuation due to stress induced migration it is sufficient that the degeneracy between previously equivalent sites be removed by uniaxial stress or, more generally, that the equilibrium distribution between sites be altered by uniaxial stress. This condition will be met (except in special directions of high symmetry) by the interstitial sites of all materials of interest as ionic conductors.

The ultrasonic absorption coefficient is given by

$$\alpha = \frac{C_\infty - C_0}{2C_0 s} \; \frac{\omega^2 t}{1 + \omega^2 t^2}$$

where t is the mean jump time, ω the circular frequency, $C_\infty - C_0$ the difference between the infinite frequency and zero-frequency values of the elastic modulus. The frequency dependence of α allows one to deduce C_∞ and t; the activation energy can be deduced from the temperature-dependence of t. The value of $C_\infty - C_0$ is approximately proportional to the number of interstitials. The elastic moduli are of course directly deducible from the density and the measured velocity of sound (s).

Nuclear Magnetic Resonance (NMR) Ion Mobility Studies (New)

Faculty Supervisor: John L. Bjorkstam
Professor, Electrical Engineering

Graudate Assistant: C. H. Wei
Predoctoral Associate I

Objective: To use nuclear magnetic resonance (NMR) methods for studying ionic motion in potential solid electrolytes.

During the six-month period covered by this report we have begun a major redirection of the work on NMR atomic motional studies from ferroelectrics to solid electrolytes. This is in keeping with a developing multidisciplinary attack on the solid electrolyte problem at the University of Washington. Expertise which has been developed in relating spectrum, spin-lattice (T_1), and spin-spin (T_2) relaxation times to motional effects near phase transitions in ferroelectrics will be directly applicable to the solid electrolyte problem.

Our initial objective is to develop a relatively simple NMR method for directly measuring the self-diffusion coefficient and mobility of ^{23}Na, ^{7}Li, ^{19}F and ^{1}H nuclei in super ionic conductors. Motional narrowing of NMR lines has been observed in such materials,[1] and interpreted in terms of a theory of Hendrickson and Bray.[2] In some cases inference can be made from these studies as to whether the motion is long range (as desired), or simply a local "rattling around." However, the results are far from being unequivocal.

NMR spin-echo methods, which have proven extremely useful for self-diffusion measurements in liquids, have not been applicable to usual diffusion rates in solids. However, the pulsed magnetic field-gradient method[3] seems to hold promise for measurement of the diffusion rates necessary if a material is to be a useful solid electrolyte. Success of the method does depend upon the ratio between T_1 and T_2. Our initial measurements will be of these parameters in order to evaluate the potential success of developing the spin-echo measurement capability. At the same time we have been giving consideration to CW-methods. These basically involve T_1 and line-shape measurements in the presence of applied stationary, and time-varying, magnetic field gradients, while at the same time inducing ac-currents in the sample. Initial theoretical considerations with respect to success of the method are encouraging. The cw-method is expected to involve more simple apparatus.

Mr. Wei began work on the project in early spring of 1973. While he has been developing expertise with respect to NMR techniques, he has been supported by a teaching assistantship in the Department of

Electrical Engineering rather than by the CMR grant. At the same time he has designed and built a temperature control system which will be necessary in our future work. Mr. Wei will begin to receive support from the CMR grant on June 16, 1973.

References

1. W. L. Roth, S. P. Mitoff, and R. N. King, Final Report, NASA Contract NAS3-15692, September 1972.

2. J. R. Hendrickson, and P. J. Bray, *Jour. of Magnetic Res*. *9*, 341 (1973).

3. J. E. Tanner, *Jour. of Chem. Phys*. *52*, 2523 (1970); K. J. Packer, C. Rees, and D. J. Tomlinson, *Molecular Phys*. *18*, 421 (1970).

Grain Boundary Effects in Beta Alumina (New)

Faculty Supervisor: Alan D. Miller
Assistant Professor, Ceramic Engineering

Graduate Assistant:

Objective: (1) To develop techniques for fabricating sodium or potassium beta-alumina bicrystal specimens, preferably with controlled boundary orientation and tilt or twist angles. (2) To determine the spatial distribution of the akali ion for a system in steady ionic conduction across an interposed grain boundary. (3) To measure the ionic electrical conductivity as a function of grain boundary mismatch.

The first phase of the program will involve procuring or manufacturing bicrystal specimens. Initially it may be possible to obtain small bicrystal specimens of low purity by selecting large grained regions of refractory shapes which contain beta-alumina. These specimens would allow limited investigation of alkali distribution provided the sodium beta-alumina could be converted to the potassium form.

The fabrication of single crystals of these materials will be investigated with respect to available methods, whether internal or external to the university. It is felt that fabrication of bicrystals is best approached from the point of view of joining of two single crystals of known orientation rather than growth of the bicrystals directly. Our experience with α-alumina bicrystals fabrication will be of great value here.

The second phase of the program will involve the investigation of silver distribution by x-ray spectrometry using the scanning electron microscope with energy dispersive x-ray capability or the electron beam microprobe. This investigation will involve establishing a steady ion current through a bicrystal specimen, stopping the flow rapidly and determining the distribution of the silver ions.

The third phase of the program is less well defined at this point and will depend to a great extent on whether satisfactory bicrystal specimens of varying boundary mismatch parameters can be obtained. It will require the construction of an AC or DC conductivity appartus.

Appendix A

PAPERS AND PUBLICATIONS

PAPERS PUBLISHED

"Oxygen Solubility in ZrC," S. K. Sarkar, A. D. Miller, and J. I. Mueller, Journal of the American Ceramic Society, 55, [12], 628-630, (1972).

"Sintering of Silica Fiber Compacts," T. J. Ormiston and O. J. Whittemore, Jr., American Society Bulletin 52, 3, 247 (1973).

"Graphitization Studies on Fluidized-Bed Pyrolytic Carbons," R. L. Beatty and D. B. Fischbach, Preprints -- Carbon '72 (Duetsche Keramische Gesellschaft, June 1972) pp. 127-9.

"Graphitization Kinetics of Fluidized-Bed Pyrolytic Carbons," R. L. Betty and D. B. Fischbach, Extended Abstracts and Program, CONF 730601 (National Technical Information Service, May 1973) pp. 30-1.

"Measurement of Dihedral Angles by Scanning Electron Microscopy," G. Achutaramayya and W. D. Scott, Journal of the American Ceramic Society, Vol. 56, No. 4, April 73, pp. 230-231.

Appendix B

GRADUATE DEGREES AWARDED

MASTER OF SCIENCE

Stephen VonTalge, M.S., Ceramic Engineering, June 1973

DOCTOR OF PHILOSOPHY

John M. Rusin, Ph.D., Ceramic Engineering, June 1973

PAPERS PRESENTED

"The Magnetic Behavior of Carbon Materials," D. B. Fischbach, Seminar, Material Div., Royal Aircraft Establishment, Farnborough, U.K., 21 June 1972.

"The Magnetic Behavior of Imperfect Graphities," D. B. Fischbach, Solid State Physics Seminar, University of Washington, 9 February 1973.

"The Relationship of Structure to Properties of Carbon Materials," D. B. Fischbach, Ceramic Engineering Seminar, Joint Center for Graduate Studies, Richland, Washington, 10 April 1973.

"Graphitization Kinetics of Fluidized-Bed Pyrolytic Carbons," R. L. Beatty and D. B. Fischbach, paper #CG-5, 11th Biennial Conference on Carbon, Gatlinburg, Tenn. 4-8 June 1973.

"The Graphitization Process," D. B. Fischbach, Lecture/Seminar, presented at the Second Industrial Carbon Science and Technology Course, Department of Metallurgy, University College, Swansea, Wales, U.K., 19 June 1972.

"Graphitization Studies on Fluidized-Bed Pyrolytic Carbons," R. L. Betty and D. B. Fischbach, paper # P 17, Carbon '72 Conference, Baden Baden, W. Germany, 26-30 June 1972.

"Polygonized Boundaries in Alumina: Formation Kinetics and Interfacial Energies," G. Achutaramayya and W. D. Scott, 75th Annual Meeting of the American Ceramic Society, Cincinnati, Ohio, May 2, 1973.

CERAMIC MATERIALS RESEARCH SEMINARS

December 16, 1972 - June 15, 1973

"Heat Content and Heat Capacity of Zirconium Carbide as a Function of Temperature and Carbon Content," John A. Negrych, Predoctoral Research Associate, University of Washington.

"Self Diffusion and Impurity Diffusion in Non-Stoichiometric Compound," Dr. Suren Sarian, American University in Cairo.

"Sintering of Silica Fiber Compacts," Thomas J. Ormiston, Research Assistant, University of Washington.

"Analastic Behavior in Barium Titanate," Stephen F. VonTalge, Research Assistant, University of Washington.

THESES PUBLISHED

"Thermoluminescence of Pure and Doped Sapphire"
John M. Rusin, Ph.D. Ceramic Engineering

"Analastic Behavior in Barium Titanate"
Stephen VonTalge, M.S. Ceramic Engineering

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