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BES Newsletter

CERAMICS: SCIENCE OF PROCESSING

Materials and Molecular Research Division
Lawrence Berkeley Laboratory
University of California

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EDITORIAL

The BES Newsletter

L. C. De Jonghe

This Basic Energy Sciences Newsletter serves as an information exchange between researchers working on the scientific aspects of processing and the Division of Materials Sciences in the Office of Basic Energy Sciences of the Department of Energy. It gives a concise description of the program scope of the various BES-DOE supported research projects on processing, cites new results, and lists recent publications and presentations that have resulted from the DOE sponsored research. From the scope of the different programs it is apparent that "science of processing" spans several disciplines. The Newsletter, therefore, provides a means of interdisciplinary exchange. The limited number and the range of the projects also indicates to what extent DOE-BES is supporting research in the crucial aspects of ceramic technology. It should be expected that the number of contributors to this newsletter will expand in the future.

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Program Scope

The work involves primarily a study of precipitation in aqueous solution with the goal of being able to determine, from process conditions, the physical characteristic of the resulting precipitate. In particular, work is being performed on those materials which are used in the preparation of ceramic powders. Particular properties being studied are surface area, agglomeration, degree of adhesion of the agglomerated particles, and particle size distribution.

Recent Results

So far, work has been performed on the precipitation of ammonium polyuranate and on the precipitate of yttrium hydroxide.

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The basic approach to the theory has been to use the concept of the population balance, modified to account for the presence of agglomerated particles, to model the size distribution functions. The major physical processes involved are particle nucleation, growth, and agglomeration, all of which are functions of the operating variables for the precipitator (a continuous mixed suspension-mixed product removal unit). The study is part of a larger interdisciplinary program which involves careful modeling and intermediate product characterization of each step in the preparation of ceramics. Ultimately the goal is to be able to prepare ceramic products with uniformly reproducible properties by identifying the effects of each step in the preparation process on the properties of the final sintered ceramic product. The present work involves the preparation and characterization of the powder. It is planned to prepare a series of ceramic powders with systematic variations in properties so that these powders can be provided to ceramists for studying the subsequent process of sintering. Theoretical and experimental work is also underway on modified sol-gel techniques and on preparation of powders by vapor phase reactions.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

BASIC RESEARCH IN CRYSTALLINE AND NON-CRYSTALLINE CERAMIC SYSTEMS: PROCESSING RESEARCH

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Program Scope

The program addresses a broad range of fundamental questions in fabrication of ceramic materials. The subjects investigated include microstructural development during sintering, grain boundary-pore and boundary-impurity interactions, surface diffusion, role of agglomeration in densification, diffusion induced grain boundary migration, and sintering of covalent materials.

Recent Results

Hot Stage SEM Study of Microstructural Development (WDK). A hot stage has been constructed to be used in conjunction with an ISI-II scanning electron microscope. The hot stage is capable of achieving a temperature of 1600°C in a couple of minutes. Magnification can be varied between 10x and 5000x. Low magnifications have allowed for the statistical analysis of shrinkage, and high magnifications permitted the observation of changes in morphology. The first investigations are being carried out on magnesium oxide because it has a high secondary electron emission coefficient at low accelerating voltages.

Work is underway in determining the mass transport mechanisms responsible for the early stages of magnesium oxide sintering, which appears to be dominated by surface diffusion phenomena.

Breakaway Grain Growth in Magnesia Doped Alumina (RLC). The rates of grain boundary migration in the presence of pores and solute atmospheres are being considered. A num-

ber of models for grain growth in pore containing material have been examined. It appears that there is an underestimate of the possible drag force of pores or particles and grain boundaries in the Zener model. New modeling is therefore needed for the evaluation of the maximum drag force between pores or particles and grain boundaries as a function of the equilibrium dihedral angles. It has been shown qualitatively that the effect can be large, i.e., that equilibrium dihedral angles less than 180° will give larger drag forces than does Zener's model. Utilizing the model in its present form, the maximum velocities have been assessed by which the pores could migrate by either lattice diffusion or by surface diffusion. The lattice diffusivity was taken from our creep data for the magnesia saturated case; the surface diffusivity was taken from previous data on grain boundary grooving. Using the average curvature from the average grain size measurement, an assessment of the maximum grain boundary was calculated by assuming that boundary migration is intrinsic based on boundary diffusivities taken from the creep data in the boundary diffusion controlled regime. The comparison shows that the boundaries have potential for orders of magnitude higher migration velocities than do the pores. While segregation of magnesia to the grain boundaries has not yet been detected experimentally, it is possible that very small amounts of it may reduce the grain boundary mobility significantly so that pore breakaway is avoided. The main point in further considerations of the grain boundary movement in magnesia containing alumina is that a combination of effects, solute effects as well as surface energies, grain boundary energies, and diffusion coefficients, and pore mobilities should be considered simultaneously rather than individually.

Grain Boundary Grooving and Surface Diffusion on Aluminum Oxide RLC). Grain boundary grooving studies have continued during the past year primarily on LUCALOX lamp tubes. The results of these experiments are in reasonable accord with our previously reported values. At higher temperatures (1450-1500°C), however, only the larger values agree with those from a previous study on LUCALOX by Robertson and Ekstrom. A possible explanation is that differing impurity levels are responsible. Auger spectroscopy has been used to characterize the surface composition. To date, no surface excess of MgO or any other impurity has been noted for the system.

Ceramic Fabrication (RLC). It has been long recognized that the preparation of powder compacts for sintering to high density without significant grain growth, would require elimination of the interagglomerate porosity that is usually present. This should hypothetically involve the use of mono-dispersed deagglomerated powder coupled with a fabrication procedure that will yield a compact of uniform density with a small and narrow pore size distribution.

We have been studying the deagglomeration behavior of some conventional raw materials by ultrasonic dispersion and by ballmilling. Using commercial alumina raw materials of small particle size (less than 1 micron) we have studied the influence of the times required for dispersion by ballmilling vs those required by ultrasonic dispersion. In relatively short times, ultrasonic dispersion has been found to give relatively good dispersion of the powder. The experimental techniques are being improved by using a sapphire tipped wave guide when highly abrasive powders such as alumina are being used.

With these dispersed powders, we have studied conventional slip casting and also consolidation by agitation of the thixotropic gel which forms upon initial water extraction. The densities of as-fabricated slip case compacts have been increased to approximately 65% theoretical density. By agitation of the thixotropic gel, the average bulk density has been increased to approximately 73%, although, at this stage, the bulk densities in those compacts are nonuniform. The more densely packed regions of these compacts are found to sinter to high density at relatively low temperatures and times, as expected.

Model Experiments on Sintering With Gold (RLC). We have obtained samples of a gold powder from DuPont that consists of virtually monodispersed, one micron metal spheres. This material, at least form the standpoint of geometry, is an excellent model candidate for studying sintering kinetics and diffusion through direct observation of neck growth rates in the scanning electron miroscope. The observations made so far have shown:

1. Substantial initial stage sintering characterized by easily seen neck growth between spheres takes place at temperatures in the range of 150 to 300°C, of times at one hour or less.

2. This effect is mainly one of coarsening, since virtually no center-to-center approach of spheres was observed at these low temperatures. A percentage of the spheres show evidence of undercutting near the neck surfaces.

Experiments on Diffusion Induced Grain Boundary Motion (RLC). Crystals of MgO were packed in pre-equilibrated Al_2O_3 saturated $MgAl_2O_4$ powder in a platinum crucible and heated in air at 1700°C for 9 hours. The diffusion anneal was followed by a precipitation anneal at 1150°C for 24 hours. The samples then were cleaved along the grain boundaries and examined in the high resolution scanning electron microscope for presence of spinel precipitates. The analysis showed the presence of the spinel precipitates along the grain boundary, with no detectable grain boundary movement. The aluminum profile across the boundary was found to be symmetrical. While in certain metal-solute systems grain boundary migration can be induced by chemical diffusion along grain boundaries, the effect was not observed in the system at hand because the grain boundary diffusivity to lattice diffusivity ratio is on the order of three. Much higher ratios are required to induce grain boundary migration by diffusion. Alternatively, an explanation for the absence of diffusion induced grain boundary migration in this system may be that oxygen, rather than aluminum and magnesium, controls grain boundary diffusion and grain boundary motion.

Sintering of Covalent Materials (RLC). It is the objective of this study to investigate the sintering mechanisms of covalent materials such as silicon carbide and silicon nitride. Silicon has been chosen as a model material for several reasons: impurity solubilities and their acceptor or donor levels are known for many dopant elements; diffusion data are available for impurities; self-diffusion mechanisms have been studied to some extent; and silicon is available in very high purity. Silicon powders may coarsen either by vapor transport or by surface diffusion, depending on chemistry and particle size. Grain boundary groov-

ing experiments for pure silicon performed by ourselves and by Robertson, have shown that surface diffusion dominates over vapor phase transport. This is in contrast to some results obtained by Greskovich et al. It is, however, possible that in his case vapor phase transport of silicon was enhanced by the reaction of Si with the aluminum oxide crucible. Impurities can significantly effect these types of processes. It is interesting to note that some systems in which diffusion induced grain boundary migration has been observed also show activated sintering. Nickel activated sintering of tungsten is a prime example of this. We have come to the following conclusions regarding the sintering of silicon:

1. Coarsening occurs by surface diffusion in pure silicon for all particle sizes of interest.

2. Chemical vapor transport SiO can dominate neck growth and lead to large weight losses under certain conditions.

3. Boron seggregates to silicon surfaces. Its role in sintering appears to be to reduce surface diffusion.

4. Diffusion induced dislocations may provide the means to enhance the densification process.

The concepts derived from the silicon work should be applicable to silicon ceramics. The effects of dopants, and the manner in which dopants are added on the coarsening process will be followed by surface area measurements and SEM microstructure characterization of powder compacts. Lattice parameter measurements should give an indication of the ability of a dopant or combination of dopants to induce lattice strains and thereby activate sintering.

PHYSICS AND CHEMISTRY OF PACKING FINE CERAMIC POWDERS

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One of the most important fabrication techniques is densification of fine powders; thus, this research program focuses on model studies and analyses which will make the most significant impact on further development of this technology by better understanding the underlying principles. The sintering paradigm for complete densification of a single phase ceramic has three basic elements:

1. The ideal characteristics of the starting powders are: small size (<1 μm), narrow size distribution (monodispersed), non-agglomerated, equiaxed, and phase and composition pure.

2. The packing of the fine powders should result in: no particle density gradients, no incorporation of foreign particles, and as high a green density as possible. Binders and dispersants should be easily removed before pore closure in order to keep the purity.

3. For densification of the powder compact to occur with control over the resulting microstructure, the thermodynamic variables, temperature, pressure and composition (dopants), must be chosen such that pore removal rather than pore coarsening or just pore shape change occurs. In addition, grain boundaries must be pinned at the pores until densification is complete.

By combining the science of ceramics and the science of colloids it is possible to understand the basic principles of the first two elements of the paradigm and thereby to understand the physics and chemistry of microstructure control in the sintering process. Colloid chemistry provides the principles for controlling the dispersion of the ceramic particles and their subsequent controlled flocculation into a uniformly packed body. There are major technological consequences of understanding and then controlling the powder and powder packing:

1. The microstructure can be reliably reproduced.

2. There is a total elimination of warping and cracking in densified pieces.

3. Complex parts can be reproducibly sintered to final shape without grinding and finishing steps.

4. Sintering aids are less likely to be required.

5. Very fine grained microstructures are obtainable which may ultimately give improved mechanical characteristics (e.g., superplasticity).

6. The conversion of a material by reaction sintering, e.g., nitriding silicon, will yield higher densities and larger conversion ratios than in uncontrolled packing.

7. The sintering time and temperature will be reduced.

Program Scope

The purpose of the proposed research is to improve our understanding of the fundamental principles of powder processing by bringing together three, seemingly unconnected areas: (1) stability of colloids, (2) formation and ordering of monosized particles, and (3) sintering paradigms. The interrelationships of these disciplines are important; for example, indiscriminate control of the particle dispersion by surface adsorbed ions may result in poor sintering (grain boundary or bulk diffusion) behavior.

We have chosen two particulate systems, TiO_2 and Si_3N_4, because of their different characteristics. Titanium dioxide dispersions can be studied in aqueous solutions, while Si_3N_4 must be studied in non-aqueous liquids because of the reaction which forms SiO_2 surface layers. Steric stabilization using macromolecules in the non-ionic solutions will also be examined. Titanium dioxide has further advantages because much is known about dispersion and adsorption onto fine particles. Silicon nitride has enormous technological value as a high temperature structural material, so these studies could have important direct applications. It must be reemphasized, however, that the purpose of our research is generic processing to establish principles applicable to any ceramic system. The five topics to be researched are:

1. Formation and dispersion of monodispersed TiO_2 and Si_3N_4.

2. Studies of order-disorder in monosized sols of Si_3N_4 and TiO_2.

3. Theoretical analyses of ordered colloids with a distribution of particles sizes.

4. Coagulation of ordered dispersions.

5. Sintering of particle compacts.

In the first six months of the program, which started March 1, 1980, two of the five topics have been started: (1) formation and dispersion of monodispersed TiO_2; and (2) a theoretical analysis of ordered dispersions.

MICHIGAN TECHNOLOGICAL UNIVERSITY

EFFECTS OF CRYSTALLIZATION OF GRAIN BOUNDARY PHASES ON HIGH TEMPERATURE STRENGTH OF SILICON NITRIDE CERAMICS

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Program Scope

In this new program, the role and the mechanisms are studied of nucleating agents on crystallization of the silicon-oxinitride containing grain boundary phases which are formed during the processing of silicon nitride and SiAlON ceramics. The microstructure and the phase identity are determined in sintered and in hot-pressed specimens. A variety of analytical techniques are employed, including x-ray defraction, scanning transmission electron microscopy, electron energy loss spectroscopy, and fractography.

OAK RIDGE NATIONAL LABORATORY

PROCESSING STUDIES OF STRUCTURAL CERAMICS

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There are applications in energy technology such as components for coal conversion systems as well as requirements for metal cutting tools and mining drill tools where advanced structural ceramics, based on non-strategic materials, are needed. The trims in pressure let-down valves required for direct coal liquefaction processes and valve parts in gasification systems are certainly of particular interest because of the importance of the material durability to the economics of these synthetic fuels. Materials for these applications must have high erosion resistance to high velocity coal slurries or particle laden gas streams. State-of-the-art materials which have performed best to date in these applications are cobalt-bonded tungsten carbides. The hard phases in this type of material which provide the required hardness and erosion resistance are generally quite refractory and due to their significant covalent bonding, are very difficult to sinter into dense monolithic ceramics of sufficient strength and toughness. In many cases, the hard phase, in single phase polycrystalline form such as tungsten monocarbide, has a relatively low fracture toughness, which

can seriously limit the potential usefulness of the material. Use of metal based bonding phases can allow fabrication of materials at temperatures well below those necessary for densification of single-phase material, as well as provide increased fracture strength and toughness with densities sufficient for technological use.

Hard structural ceramics such as cobalt bonded tungsten carbide acquire several of their more desirable properties because of the presence of cobalt-rich secondary phases. These technologically important materials contain the strategic elements cobalt and tungsten, and it is of considerable importance that alternative materials be identified. For this reason and the fact that state-of-the-art materials may not have the durability required for use in coal conversion system components, it is important that alternative materials be studied. There are several hard phases which offer potential for displacing tungsten carbide based materials for certain critical applications, including selected diborides, such as TiB_2 and ZrB_2.

Program Scope

Processing studies have started recently on selected systems containing TiB_2 and a transition metal to determine the relation between fabrication variables and properties of the resultant ceramics. Areas of study include elastic modulus hardness, flexure strength, thermal diffusivity, erosion resistance, wear resistance, and the ability of the ceramics to cut selected alloys. Presently, major emphasis is concentrated on the systems TiB_2-Ni, TiB_2-Ni-Cr and $(Ti,Cr)B_2$-Ni to identify relationships between initial boride to nickel ratios, starting boride particle size and morphology, hot pressing variables, and the final properties of the ceramics. Compositions in the systems TiB_2-Ni, $(Ti,Cr)B_2$-Ni, and TiB_2-Ni,Cr are presently being studied from 10 to 20 mole percent nickel. Powders of the boride and nickel are blended, compacted and hot pressed at temperatures near 1450°C at pressures of 12 MPa for times up to eight hours. During the hot pressing, the nickel, or nickel + chromium and boride form a liquid phase which crystallizes during subsequent colling.

The strength, hot hardness, elastic modulus, and thermal diffusivity of these materials are being determined as functions of the processing variables. In addition, the erosion and wear characteristics of the experimental materials are being determined by means of hot coal slurry, particle erosion, and quantitative wear tests. Structure of the boride ceramics is being determined by means of x-ray diffraction, SEM, optical microscopy, and analytical electron microscopy.

Results to date indicate that after fabrication, the nickel and nickel/chromium have become incorporated into various titanium and boron bearing phases located in grain boundaries between the boride grains. Correlations of bulk properties are being made with the secondary phase structures, compositions, and distributions. Erosion test results to date indicate that these early experimental materials approach the performance of the best commercial cobalt bonded tungsten carbides. Room temperature diamond pyramid hardness values above 21 GPa (2100 kg/mm^2) at 20 N (2 kg) have been measured for these materials. Erosion and wear results obtained for these materials will subsequently be reported in the BES Erosion-Wear Research Newsletter.

PURDUE UNIVERSITY

MECHANISM OF ELEVATED TEMPERATURE RUPTURE IN SINGLE PHASE CERAMICS: PROCESSING ASPECTS

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Program Scope

Fabrication of High Density Specimens. We are studying the growth of cavities in single phase ceramics under tension and with pressurized pores. Toward this end, we will fabricate very high-density, formed specimens of uniform microstructure without microcracks.

Hot-Pressing and Swelling of Ceramics. We have been studying hot isostatic pressing of ceramics, both as a fabrication process, and as a deformation process in service. Although the initial stages were funded by the NRC, some work is continuing under DOE sponsorship to examine stoichiometry and grain size effects.

Gas Entrapment in Ceramics. Although end-point densities in sintered bodies are often attributed to entrapped gases or exaggerated grain growth, the entrapped gases are difficult to identify and quantify. We are conducting swelling and gas release experiments to reveal the amount and type of such gases using a quadrupole mass spectrometer.

ROCKWELL INTERNATIONAL SCIENCE CENTER

SINTERING PHENOMENA OF NON-OXIDE SILICON COMPOUNDS

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Program Scope

Studies are underway to understand the volatilization phenomena associated with non-oxide silicon compounds, which presently inhibit the sinter ability of single phase powders and hinders densification when a sintering aid is used.

Work is also performed on the liquid phase sintering of non-oxide silicon compounds containing a sintering aid. The over-all goal is to understand the interrelation between phase equilibria and fabrication parameters with emphasis on the silicon nitride and silicon carbide systems. Additionally, work is performed on the Si_3N_4 - SiO_2 - Y_2O_3 phase equilibria. Diffusion processes occurring in these systems are also studied. The techniques that are employed in this investigation include scanning transmission electron microscopy as well as analytical electron microscopy.

Recent Results

Compositional and morphological information has been obtained using the transmission electron microscope, indicating that the non-crystalline phase in hot pressed silicon nitride alloy can undergo phase separation. The compositional range determined

for the phase separation is close to the known miscibility gap in the silica-magnesia pseudo-binary system. Crystallization of silicon oxinitride and $MgSiO_3$ from the non-crystalline phase is also evident, suggesting that it can contain some dissolved nitrogen and that the integranular phase may be crystallizable.

The elemental composition of the noncrystalline intergranular phase in three magnesia fluxed hot-pressed silicon nitride alloys was determined by x-ray microanalysis and by electron energy loss spectroscopy in a transmission electron microscope. The composition of the intergranular phases was found to be similar in all three alloys and was close to the SiO_2-$MgSiO_3$ tieline, and contained impurities of calcium, aluminum, and chlorine. The nitrogen, however, in the non-crystalline phases was found to be below the experimentally detectable limit.

It was found that the sintering in the Si_3N_4 - $Y_2Si_2O_7$ - Si_2N_2O system only occurred in the presence of the eutectic liquid and that three processes occur concurrently during sintering: densification, the alpha to beta silicon nitride phase transformation, and the chemical reaction of SiO_2 and Si_3N_4 to form silicon oxinitride.

It was found that the weight loss encountered during this sintering of silicon nitride composite powders was due to the reaction of silicon nitride with SiO_2 resulting in volatile SiO and N_2.

A theoretical study indicated that a liquid film trapped between two compressed grains does decrease in thickness with time, but that a finite thickness is approached in practice as time tends towards infinity. The change in the thickness of the liquid should alter the flux of diffusing solute in the model proposed for liquid phase sintering by Kingery.

LAWRENCE BERKELEY LABORATORY UNIVERSITY OF CALIFORNIA

REFRACTORIES PROJECT: CHEMICAL-MECHANICAL STABILITY

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To permit efficient high temperature operation of coal technology systems, reaction chambers must be lined with refractory materials to insulate external metal pressure vessels thermally, to protect them against chemical attack, and to minimize heat losses. Two systems of lining designs are presently used. One is a layer of dense alumina castable refractory (calcium aluminate bonded alumina cement) at the hot face, with a layer of a less dense, high alumina castable between it and the pressure vessel wall. An alternative design uses dense alumina blocks. In these refractories, silica is undesirable since it is not sufficiently inert. Silica is, however, present as a common impurity in nearly all commercial refractories.

The conditions in the reaction vessel can be extreme. Among the observed failure modes one finds:

1. Thermal shock leading to spalling. This is more severe for dense ceramics than for porous ones.

2. Erosion by ash and coal particles.

3. Molten slag attack.

4. Attack by water, hydrogen, and other corrosive gases at high temperatures.

The reaction of refractories with gases such as steam at high temperatures and high pressures can take many forms. For example, silica can be transported readily in superheated steam at high pressures. Steam can also hydrate calcium aluminate bonding or intergranular phases, thereby redistributing them and weakening the refractory. The hydration reactions become less serious at higher temperatures and more serious at higher pressures. Most studies to date, however, have been done at temperatures below 1000°C. It is, therefore important that the range of investigations of the properties of the calcium aluminate refractories be extended to temperatures that are relevant to the coal gasification technologies.

The attack of refractories by slags represents also a singificant problem. The nature and the kinetics of slag-refractory reactions and their effect on the mechanical integrity of the ceramics are poorly understood and need to be explored further. The refractories are under some load in the reaction chambers and creep processes in conjunction with chemical degradation will occur. Little is known about the mechanical properties of two phase refractories. Both the role of the integranular or bonding phases and of the porosity have to be established.

Program Scope

This new, multi-investigator program has three related main activities: (1) densification-processing, (2) chemical properties, and (3) mechanical behavior at high temperatures. All research is centered around the $CaO-Al_2O_3$ system.

Densification Studies. Densification of aluminum oxide containing measured amounts of calcia: Of special interest are the elucidation of liquid phase sintering phenomena, the clarification of pre-eutectic densification phenomena, and the determination of mass transport phenomena and their comparison with high temperature creep data.

Chemical Studies, Microstructure and Kinetics. Effect of high temperature $H_2O/H_2/H_2S$ exposure on grain boundaries and intergranular phases in dense Al_2O_3 containing measured amounts of CaO: Of special interest will be the chemical microanalysis by scanning transmission electron microscopy (STEM) of regions affected by the corrosive gases, and the high resolution imaging of affected grain boundaries.

Effect of high temperature H_2O/H_2 exposure on second phases and on phase redistribution in calcium aluminate bonded alumina refractories: Alumina castable refractories have shown most promise in service in several liquefaction and gasification systems. Of special interest are reactions of the bonding phases with steam, and the redistribution of the phases. Exposure at high temperatures will be followed by

a detailed microanalysis with high voltage electron microscopy. The use of high voltage transmission electron microscopy at 1.5 MeV will permit the porous samples to maintain much of their integrity since thick electron microscope specimens can be used.

Attack by simulated liquid coal slags of dense Al_2O_3 containing measured amounts of CaO: Of special interest here is the possibility of forming spinel reaction products at the slag/refractory interface, and the potential role of grain boundary and intergranular phases in modifying the spinel layer. The presence of SiO_2 is also important and will be investigated.

Mechanical Studies, Creep and Chemical Effects. Creep deformation and creep-fracture studies of dense Al_2O_3 with measured amount of CaO: Of special interest are the influence of impurities and intergranular phases on local mass transport and on cavity growth, as affected by the external stress and by the local environment. The study will involve theoretical determinations of mass transport, and experimental observations of cavity morphology in relation to second phases, as functions of stress level and of strain history.

Low-stress creep of calcium aluminate bonded alumina two phase refractory: Of special interest are the influence of calcium aluminate bonding phases and of the extensive initial porosity. Possible nonlinearities in deformation associated with interface behavior are of special concern at low stress levels.

The results are expected to provide the basis for developing a fundamental approach to the prediction of mechanical and chemical interactions and stability in refractories or high temperatures and to the processing of two-phase ceramics.

UNIVERSITY OF CALIFORNIA, DAVIS

AN INVESTIGATION OF THE ROLE OF SINTERING IN GAS-SOLID INTERACTIONS

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Program Scope

This new program is an investigation of the role of sintering in the kinetics of gas-solid interactions in powder compacts. The influence of surface transport and bulk transport sintering on the kinetics of dissociation reactions of the type $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$ and of reduction reactions of the type $FeO(s) + H_2(g) \rightleftharpoons Fe(s) + H_2O(g)$ will be investigated. Morphological changes (surface area, pore size, and overall porosity) will be measured and related to changes in the rates and reversibility of interactions of the types indicated above.

LATE ENTRY

AMES LABORATORY

CERAMIC PROCESSING

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PROGRAM SCOPE: The objective is to study the individual steps (and their interrelationships) in the production of highly-sinterable oxide powders derived from inorganic precursors. Current emphasis is being placed on two topics: (a) Investigation of the influence of precipitation variables on distribution of sizes and state of agglomeration of hydroxide precursors. (b) Investigation of the changes in precursor characteristics during the crucial dewatering step following precipitation. The two dewatering procedures being studied are the Ames Laboratory acetone-toluene process [1, 2], and dewatering under controlled humidity conditions.

Highly-sinterable powders of Y_2O_3, rare-earth oxides, ThO_2, pure and rare-earth doped ZrO_2 and HfO_2 can be produced by calcination of acetone-toluene dewatered hydroxide precursors. Controlled humidity dewatering of Y_2O_3 and rare-earth oxide precursors have also yielded highly-sinterable material.

1. U. S. Patent 4, 140, 771 (Feb. 20, 1979)
2. S. L. Dole, R. W. Scheidecker, L. E. Shiers, M. F. Berard and O. Hunter, Jr., "Technique for Preparing Highly-Sinterable Oxide Powders" Materials Science and Engineering, 32:277-81 (1978).

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