RESEARCH OPPORTUNITIES IN CERAMICS SCIENCE AND ENGINEERING

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The United States aerospace, automotive, biomaterials, chemical, electronics, energy, metals, and telecommunications industries collectively employ more than 7 million people in materials science and engineering and have sales in excess of \$1.4 trillion. Recent reports[1] have called the 1990*s* the "Age of Materials" and have concluded that the field of materials science and engineering is entering a period of unprecendented intellectual challenge and productivity. Chemical engineers, with their background in reaction engineering and transport processes, have the skills necessary to make significant contributions in this area.

A strong component of materials science and engineering is ceramics science and engineering. Although many applications of ceramics have in the past been low-tech, a vast number of new high-tech ceramics have been developed in recent years, opening up a large number of new and exciting applications for a wide variety of industries. Ceramic superconductors may provide new methods of energy transmission and new types of electronic devices. Electronic ceramics such as $BaTiO_3$ and $SrTiO_3$ are used to make capacitors and sensors. Ferroelectric ceramics can be used to produce memories for computers. A variety of metal oxides, nitrides and silicides are used in computer chips and to make substrates for the chips themselves.

Ceramics can also be used to make chemical sensors for detecting small amounts of hazardous substances for applications in hazardous waste control. They are also used as catalysts for chemical reactions or as catalyst supports in the chemical industry. These and other applications have led to a tremendous interest in the synthesis, processing, and characterization of ceramic materials in the form of powders and films.

The chemical engineering department at the University of New Mexico dramatically expanded its program in ceramics science and engineering following the establishment of a National Science Foundation-supported UNM/NSF Center For Micro-Engineered Ceramics (CMEC). Numerous research projects, many in the areas mentioned above, are now available to interested students. These opportunities are particularly interesting since demand is high for students with a background in ceramics, with fewer than forty PhD*s* being granted in the United States each year in Ceramics Science and Engineering (with roughly half of them going to foreign students).

This article briefly describes some of the research

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C. Jeffrey Brinker *received his BS, MS, and PhD degrees from Rutgers University, and joined the Ceramic Development Division at Sandia National Laboratories in 1979. He is presently a member of the technical staff and a University of New Mexico/Sandia National Laboratory professor of chemistry and chemical engineering.*

Abhaya K. Datye *received his BS from the Indian Institute of Technology, Bombay (1975), his MS from the University of Cincinnati (1980), and his PhD from the University of Michigan (1984), and has been a member of the chemical engineering faculty at the University of New Mexico since 1984.*

Douglas M. Smith *received his BS (1975) and MS (1977) from Clarkson University and his PhD (1982) from the University of New Mexico. Previous positions include Unilever Research and Montana State University. He is currently professor of chemical engineering and serves as Director of the UNM/NSF Center for Micro-Engineered Ceramics.*

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opportunities in ceramics science and engineering at the University of New Mexico and the unique interdisciplinary nature of the projects which involve investigators from chemical engineering and other departments, from centers at UNM involved in materials, and from Sandia and Los Alamos National Laboratories.

RESEARCH AREAS

The authors of this paper have extensive programs in ceramics science and engineering. Their projects span ceramics synthesis, processing, and characterization.

Jeffrey Brinker is investigating sol-gel processing of ceramics—films, fibers, powders, and bulk; physics and chemistry of film deposition from liquid precursors; defects in glasses; controlled porosity materials for sensors, membranes, and adsorbents; nanoscale materials; multifunctional composites; and fractals.

Sol-gel processing (see Figure 1) refers to the room temperature formation of inorganic materials from molecular precursors.[2] Inorganic salts or metal organic compounds dissolved in aqueous or organic solvents are hydrolyzed and condensed to form polymers composed of M-O-M bonds. These polymers may be deposited on substrates to form thin films, drawn into fibers, or cast in molds and dried to form "near-net-shape solids." Prior to drying, the structures of the polymers are often described by fractal geometry,[3] a consequence of kinetically-limited growth mechanisms such as reaction-limited cluster aggregation.[4] The properties of fractal objects may be exploited to prepare materials (films, fibers, or bulk) with precisely controlled pore structures (*e.g.,* pore size, surface area, and percent porosity). Films with controlled pore sizes[5] may be used as molecular sieves to impart steric selectivity to sensor devices or to separate a mixture of gases on the basis of size.

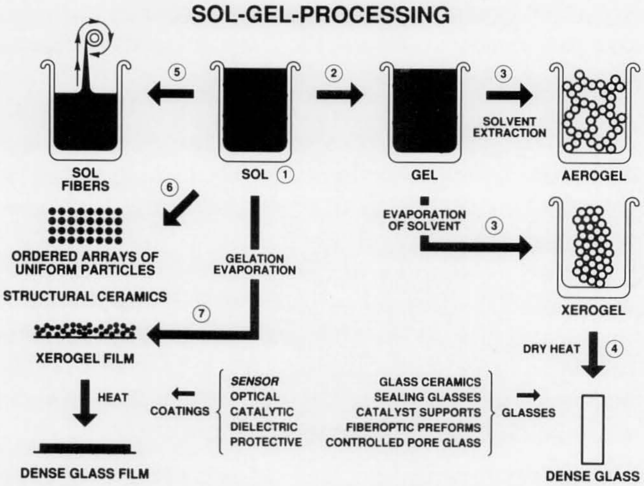

FIGURE 1. *Processes occurring during sol-gel processing of materials*

The inherent porosity of sol-gel-derived materials provides access to reagents throughout the material's interior. Surfaces may be modified by reactions with gas or liquid reagents, and secondary phases may be depositied within the pores to form nanoscale composite materials.[6] Alternatively, secondary phases may be incorporated in the liquid or sol. Under certain conditions, deposition of the diphasic sol results in a composite film in which the second phase is embedded in a dense gel matrix. Zeolite/gel composites made by this procedure can impart molecular recognition capabilities to sensor surfaces.[7]

Sol-gel-derived materials are highly metastable; their structures are dictated by kinetics rather than by thermodynamics.[2] Kinetic pathways may be exploited to prepare novel inorganic materials. Only when these materials are processed in the vicinity of the glass transformation temperature do their structures approach those of their conventionally prepared counterparts.[8]

Abhaya Datye is interested in: heterogeneous catalysis and surface science; structure and properties of thin films and interfaces in ceramics and semiconductors; and materials characterization by electron microscopy.

Phenomena occurring at the interfaces between dissimilar materials have enormous implications in materials we use every day. For instance, the strength of the bond between a metal and a ceramic determines the properties of glass metal seals as well as the high-temperature stability of heterogeneous catalysts. Sometimes a weaker interface is desired (as in a fiber-reinforced composite) to redistribute stresses at the interface and deflect cracks to make a brittle ceramic tougher. In semiconductors the performance of a device is often determined by the impurities and defects at an interface. Therefore, engineering of such complex materials requires a good understanding of the interface region and the means of tailoring the interface to achieve desired properties. Since even a monolayer of a hydrocarbon can affect the wetting of water on a solid substrate, it is apparent that interfacial properties are determined by changes occurring over the scale of atomic dimensions. It is therefore necessary to use probes having high spatial resolution as well as those that give chemical information from the near-surface region. In the research at the University of New Mexico, high-resolution transmission electron microscopy and surface-sensitive spectroscopies are used to study these materials and correlate their structure with properties relevant to their commercial applications.

One project involves the study of thin-film coatings of non-oxide ceramics and their interactions with ceramic substrates.[9] We are examining the potential of boron nitride for use as a high-temperature coating material for fiber-reinforced composites. The interaction of BN with oxide ceramics is quite strong, and BN appears to readily wet and coat these substrates. However, a detailed study[10] of the atomic structure of this interface reveals that the interatomic spacing between the BN sheets and MgO is larger than distances normally associated with chemical bonding (see Figure 2).

Other projects deal with fundamental studies of oxide surfaces in order to understand the surface chemistry involved in preparing monolayer and multilayer films of other oxides for potential catalytic applications.[11,12] Studies of surface structure in small metal particles are being conducted in the laboratory to examine the effect of pretreatments and the ceramic support on catalytic behavior.[13] Finally, the high spatial resolution of TEM is exploited to study the structure and properties of materials ranging from strained layer superlattices[14] to fine pores in oxides.[15]

Toivo Kodas is studying: the formation and processing of electronic, mechanical, and superconducting ceramic powders; laser-processing of materials; chemical vapor deposition of ceramics and metals for microelectronics applications; and aerosol physics and chemistry.

High-purity powders with controlled chemical compositions, particle size distributions, and microstructures are required as precursors for fabrication of superconducting and conventional ceramic parts. The goal of this work is to develop gas-phase routes for the formation of powders with these characteristics. Both gas-to-particle conversion and intraparticle reaction processes are being examined. Research is focused on obtaining a basic understanding of the physical and chemical processes controlling multicomponent powder production by chemical reaction, and processing these powders to produce ceramics with unique electrical, optical, and mechanical properties. Examples include $Ag/YBa_2Cu_3O_{7-x}$[16-18] for a variety of applications, $Ba_{1-x}Ca_xTiO_3$ for temperature sensors[19] (see Figure 3), mullite for electronic device substrates,[20] and BN for structural applications.[21]

Chemical vapor deposition is used extensively in

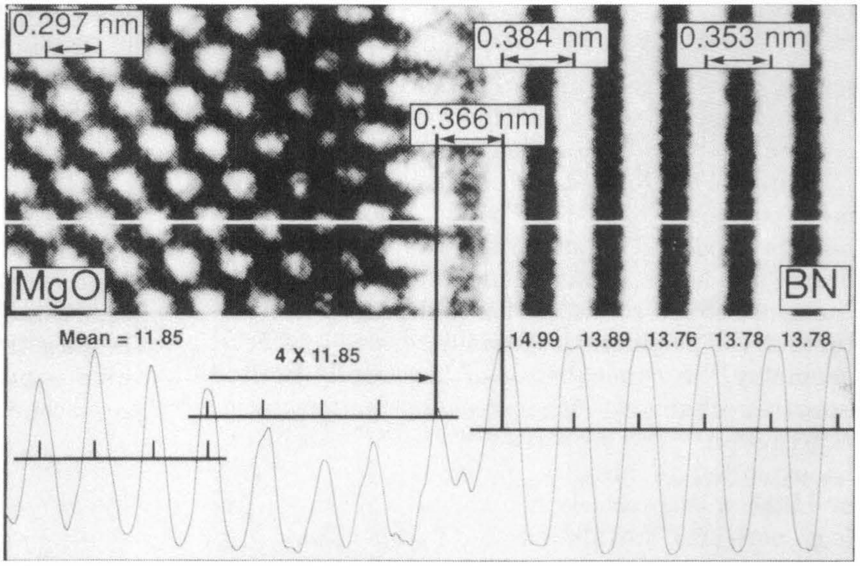

FIGURE 2. A high-resolution electron micrograph of the BN/MgO interface.[10] The array of white spots on the left corresponds to a projection of the MgO structure imaged along the <110> direction. The rows of light contrast on the right come from the basal planes of the hexagonal BN lattice. The micrograph was digitally processed to allow precise measurement of the spacing between the atomic planes. Shown above is a microdensitometer trace of image intensity along a direction normal to the interface. Spacings are indicated in mm (to an accuracy of ±1 pixel = 0.01 mm). A variation in the BN interatomic spacing is evident in the region near the interface.

industry for the formation of thin films of a wide variety of materials. This process begins with a volatile molecular species that is transported to a substrate where it decomposes and results in deposition of material with desorption of volatile byproducts. The chemistry occurring during deposition determines the deposition rate, minimum deposition temperature, adhesion to the substrate, and electronic properties. Yet the chemistry occurring during most CVD processes is poorly understood. Our research involves the use of high pressure and ultrahigh vacuum systems utilizing mass spectrometry, Auger electron spectroscopy, temperature-programmed desorption, FTIR, and Raman spectroscopy to study the surface and gas phase chemistry. The goal is to develop a better understanding of the role of chemistry in determining the properties of the deposited material. Current projects are the examination of deposition of PLZT with Radiant Technology, Cu with Motorola,[22] and $YBa_2Cu_3O_{7-x}$ with Los Alamos National Laboratories.

Aerosols (fine particles suspended in a gas) play a fundamental role in fine metallic and ceramic particle production, optical fiber production, thin film formation, and contamination control in cleanrooms. We are currently examining the interaction between the chemistry and aerosol dynamics in systems for gas phase particle production,[23-24] deposition of these particles onto surfaces to form coatings,[22] and during laser-induced deposition processes.[25]

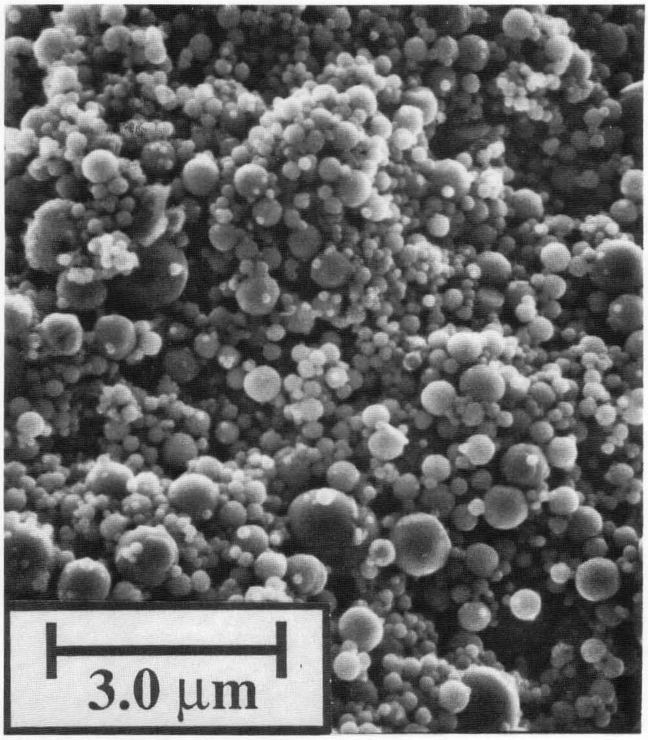

FIGURE 3. $Ba_{0.86}Ca_{0.14}TiO_3$ *particles made by aerosol decomposition.*

Douglas Smith is currently examining characterization of porous materials, transport phenomena in porous media, sol-gel, and powder processing.

The pore structure of materials is of considerable interest for a large number of applications which include ceramics processing, catalysis, membrane separations, radioactive waste isolation, and coal gasification. The basic approach is to study the physics of both established and innovative pore structure analysis tools in an attempt to extract more detailed information about porous solid systems.

Conventional techniques for pore structure analysis include mercury porosimetry, nitrogen adsorption/condensation, and microscopy (optical, scanning, and transmission electron). Each of these techniques suffers from different disadvantages which limit accuracy and preclude their use for in-situ pore structure analysis. Therefore, considerable incentive exists for the development of new techniques for pore structure analysis. Professor Smith's laboratory has pioneered the development of low-field, NMR spin-lattice relaxation measurements of fluid contained in pores as a structure analysis technique. This approach allows the study of pores of "wet" materials and allows imaging of pore structure as a function of time while the structure evolves.

In addition to pore structure analysis, the study of the physical nature of surfaces is of interest. In particular, the fractal nature of surfaces is being studied via molecular probe techniques.[26] A parallel effort using SAXS (small angle x-ray scattering) and SANS (small angle neutron scattering) is underway in collaboration with investigators at Sandia National Laboratories. The growth of fine particles and polymers in solution is studied via both SAXS and light scattering.

Using expertise in pore structure analysis, a number of ceramics processing problems are being examined. These include pore structure evolution and elimination during sintering of ceramic green bodies, dispersion of powder agglomerates, packings of powders during green body formation,[27] and pore structure development during sol-gel processing of xerogels and aerogels (both bulk[21,29]) and coatings.[30,31] Ceramic powder synthesis is conducted using a range of techniques including reactive laser ablation, sol-gel processing,[32] precipitation, and aerosol processing.[20]

CENTER FOR MICRO-ENGINEERED CERAMICS

Much of the research in ceramics science and engineering is being carried out in the National Science Foundation Center for Micro-Engineered Ceramics, which is housed in the chemical engineering department. The Center consists of fifteen professors from the University of New Mexico (seven from chemical engineering, four from chemistry, one each from mechanical engineering, physics, and geology), over ten staff members from Sandia National Laboratory, and over ten staff members from Los Alamos National Laboratory. A critical feature of the Center is the membership of more than fifteen industrial members. This allows the Center to combine the expertise of the national labs, the university, and industry to attack ceramics-related problems of interest to industry. The goals are to attack useful problems, to transfer technology between industry, the National Labs and the University, and to train students in ceramics science and engineering. A key feature of the Center is the hands-on policy for use of equipment. The Center is equipped with a variety of state-of-the-science equipment, shown in Table 1.

INTERACTIONS WITH OTHER DEPARTMENTS AND NATIONAL LABORATORIES

Another feature of the CMEC and the chemical engineering department is the extensive interactions with other departments at the university. The projects in the CMEC are interdisciplinary with faculty from chemical engineering, chemistry, physics, geology, mechanical engineering, and the national laboratories involved in each project. In addition, significant interactions occur with the Center for High Technology Materials in electrical engineering whose strength is optoelectronic materials.

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TABLE 1
CMEC Facilities

- **High-field solution and solids FT-NMR spectrometers: GE NT-360, JEOL GX-400, Bruker AC-250P, Varian 400 MHz Unity 1**
- **Low-field pulse NMR spectrometers: 10 MHz, 20 MHz, 4-60 MHz, for sol-gel and green body structure analysis**
- **Hitachi S-800 field emission SEM (20 angstrom resolution) with low Z x-ray analysis and advanced image analysis**
- **Electron Beam Microanalysis Facility, including JEOL 2000FX TEM with TN5500 EDS, JEOL Superprobe with 5 spectrometers, Hitachi S-450 SEM**
- **Electron spin resonance spectrometer**
- **FT-Infrared spectrometers: NIC-6000, Perkin-Elmer, Galaxy 6020 coupled to high-vacuum IR cell for powder studies**
- **Single-crystal and powder x-ray diffractometers**
- **Powders and Granular Materials Laboratory, includes: Autoscan-33 mercury porosimeter, Quantiment 720 image analyzer, Autosorb-1 automated nitrogen sorption analyzer, Sedigraph particle-size analyzer, Coulter Counter, 4 adsorption instruments, gas permeation apparatus, Micromeritics Accupyc 1330 - Pycnometer, Micromeritic ASAP-2000 adsorption analyzer**
- **Small-angle x-ray scattering (SAXS)**
- **Two RF high-temperature (3000°C) furnaces**
- **High-temperature thermal analysis instrumentation (TGA, DTA, DSC, Dilatometer)**
- **Laser birefringence facility for the in-situ study of stress in sol-gel and polymer processing**
- **Aerosol powder reactors including high-temperature (1700°C) and scale-up aerosol reactor for production of oxide ceramic powders (kilograms per day)**
- **Coupled TPD/Auger apparatus for surface analysis**
- **Light scattering: Spectraphysics 2000 krypton laser, Brookhaven Gonimeter, BI-2030 AT controller**
- **Nuclear Magnetic Resonance Imaging (NMRI) for in-situ studies of transport phenomena in porous materials**
- **Four gas membrane test stands.**

The extensive interactions of the chemical engineering department and CMEC with the national laboratories has numerous advantages. The strengths of SNL include electronic ceramics and glasses, while LANL is primarily involved in structural and superconducting ceramics. These skills complement the strength of the University in chemical routes to ceramics and materials characterization. Scientists and engineers at the Center and in the chemical engineering department have access to state-of-the-science equipment at the national laboratories. In addition, fellowships such as the UNM/LANL PhD fellowship are available to outstanding students with a stipend of $16-18 k/yr.

Researchers at the chemical engineering department and CMEC have access to various facilities at the national laboratories. The facilities of LANL include the Exploratory Research and Development Center for Superconducting Ceramics, the LANSCE-Los Alamos Neutron Scattering Center, the Center for Materials Science, and the Ion Beam Materials Laboratory. The facilities of SNL include the Surface Modification and Analysis Facility, Ceramics and Glass Processing Facility, SNL/LANL dedicated EXAFS lines at Brookhaven and Stanford, and a 30,000 ft^2 materials research and development laboratory which is jointly administered by UNM and SNL.

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