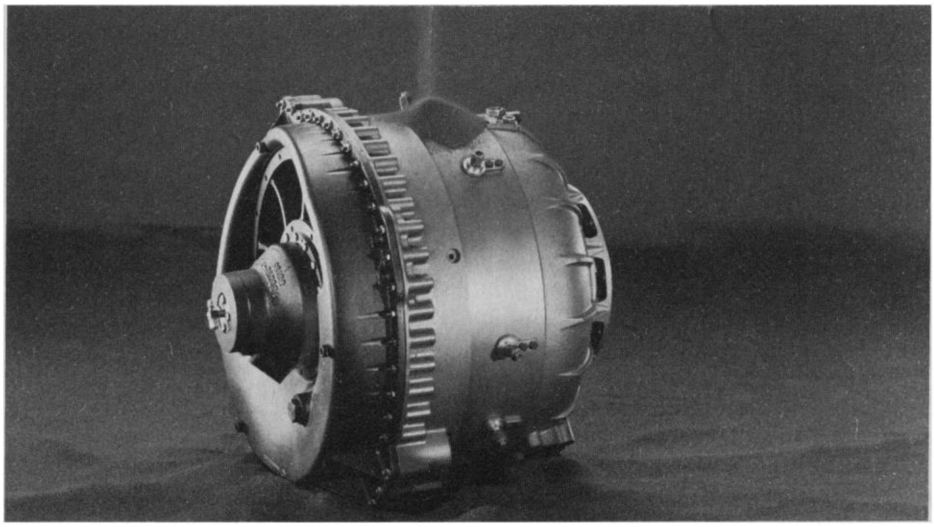
A Chemical Route to Advanced Ceramics

The secret to improving a ceramic material is to control its structure at very small length scales in an early stage of fabrication; chemistry may be the way to achieve this goal

“Physics has had its crack at ceramics; now let chemistry have its turn.” This confrontational sentiment underlies an increasingly popular approach to upgrading the properties of ceramic materials of all types, thereby providing an entree for their use in applications ranging from high-temperature engines to optical signal processors and computers to biomaterials. A symposium titled “Better Ceramics Through Chemistry” that was part of the Spring Meeting of the Materials Research Society (MRS)* provided a partial look at how this idea is faring.

Ceramics encompass most inorganic materials except metals. Both traditional ceramics, which are made from naturally occurring minerals (such as clay, silica, and feldspar) and advanced or high-technology ceramics, which may require highly purified starting materials, go through similar processing stages on the way toward the finished product. These include preparing a powder, forming the powder into the desired shape (green body), sintering the green body at high temperature (and sometimes high pressure) to obtain a dense material, and finishing the sintered body to the final shape. The new chemical approaches, such as the sol-gel processes that dominated discussion at the MRS symposium, apply in some cases to powder formation and in others to all four stages.

With a market heading toward $10 billion or more by the end of the decade, advanced ceramics are the hot commodity at the moment, and practitioners of the trade such as David Clark of the University of Florida are saying that ceramics will be to the 1990’s what polymers were to the 1970’s. The new materials tend to fall into two groups, those of interest for electrical, optical, or magnetic applications and those having outstanding mechanical or structural performance, especially at high temperatures. Sometimes both kinds of properties are needed at once, as in highly transparent window materials that can stand up to the intense laser beams envisioned for some military applications. On top of their other virtues, ceramics are less dense than metals, so parts are lighter, and raw materials are abundant.



Garrett Turbine Engine Company

Ceramic gas turbine

All of the components in the hot gas flow path of this 100-horsepower gas turbine are silicon carbide, silicon nitride, or lithium aluminum silicate ceramics. The engine housing is metal. The silica sand suggests that raw materials are abundant and inexpensive.

Right now the single largest use for advanced ceramics is in electrically insulating integrated circuit packages and substrates. A companion symposium at the MRS meeting focused entirely on this and related electronic applications. However, the “glamour” ceramics are those being developed for high-temperature engines for future automobiles. Unfortunately, the increased efficiency and reduced fuel consumption associated with operation without cooling systems and at temperatures as much as 50% higher than possible in metal engines have been touted so often for so many years that some ceramists are worried that the promise may have been oversold. Much more likely near-term uses for advanced structural ceramics are in turbochargers to boost the power of conventional automobile engines, where higher temperature and lighter weight both improve the performance, and in cutting tools, where the hardness of these materials plays an important role, according to studies by Elaine Rothman, Joel Clark, and H. Kent Bowen of the Massachusetts Institute of Technology (MIT).

In any case, advanced ceramics have been the subject of this and several other studies and reports over the last 2 years. Of particular concern is the rapid progress of Japanese research and development in these materials relative to that in the United States. Japan has been struck by “ceramic fever,” and as in other areas, notably microelectronics, companies there are committed to mounting forward-looking, sometimes cooperative, research and development programs that build on the existing pool of knowledge and to rapidly converting what they learn into marketable products. One American response was the formation last fall of the U.S. Advanced Ceramics Association, partly for the purpose of developing a sense of identity, purpose, and momentum for the industry.

Integrated circuit packages provide one motivation for the concern. Michael Kelley of the Department of Commerce told those attending a conference last July at the National Bureau of Standards on the future of the U.S. advanced ceramics industry that a single Japanese company, Kyoto Ceramics (known as Kyocera in the United States), which also makes those “new stone age” ceramic scissors and knives that are now widely available, has captured almost two-thirds of this market.

The glamour ceramics for high-temperature engines give even more cause for con-

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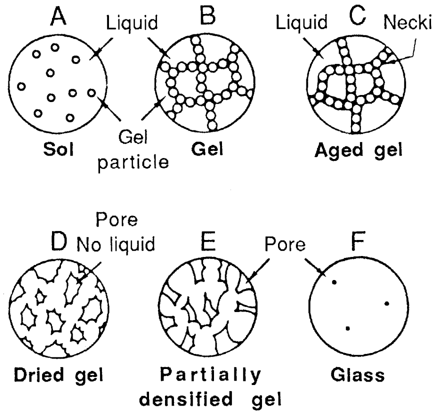
cern. Over the period from 1971 to 1985, various federal agencies spent over $150 million on advanced ceramics projects aimed at demonstrating ceramic gas turbine engines. These programs demonstrated that there is a place for ceramics, such as silicon carbide, silicon nitride, and related materials, and a joint Garrett Corporation/Ford Motor Company effort will soon test a 100-horsepower ceramic turbine engine. But there has been little emphasis on developing low-cost processing technologies. The Japanese jumped in much later, but already Nissan has begun selling, so far only in Japan and in limited numbers, deluxe model cars equipped with turbochargers having ceramic parts, while Isuzu has been offering since 1981 a similarly limited number of vehicles with diesel engines having ceramic glow plugs and precombustion chambers. The fear is that losing the race to the next generation ceramic automobile engine would have immense economic consequences.

While gaining production experience is important, putting ceramic parts in commercial vehicles is a bit of a gamble, however, because the main problem with these materials has yet to be solved. Ceramics are well known to be brittle; they deform very little before failing catastrophically. While this aspect of brittleness is an unpleasant fact of life, engineers could design parts in such a way as to emphasize the strong points of ceramics, such as strength at high temperature in structural materials, while minimizing this liability. However, brittleness has another consequence that is harder to deal with. Unlike metals, which fail under predictable conditions, ceramic parts that are for all practical purposes identical fail at quite different loads. This unpredictability is what makes engineers shy away from the use of ceramics.

Failure is statistical because the distribution of defects, such as pores and cracks, in ceramics is at present uncontrollable. Under a load, these defects act as local stress concentrators. Unlike a ductile metal, a ceramic cannot deform to relax the stress, and it has no choice but to fracture by means of a crack that propagates through the material from the defect where the stress first exceeds the failure threshold. And since every ceramic part has a different distribution of defects, the load that will generate an internal stress exceeding the threshold somewhere in the part cannot be predicted.

A way to deal with the statistics that is not satisfactory because it is so expensive is called proof testing. In essence, parts are tested up to a certain load. Those that survive are retained, while everything else is thrown away. In a recent analysis of the economics of ceramic rotors for automobile turbochargers, for example, Rothman, Clark, and Bowen at MIT estimated that the yield (fraction of good parts) is presently as low as 10%. In their model, the cost per rotor increases in a strongly nonlinear way as the yield drops. To be cost-competitive with the nickel-based alloys now used, ceramic rotors would have to be manufacturable with yields of at least 70%, conclude the authors.

As reflected in papers presented at meetings such as that of the American Ceramics Society in Chicago at the end of April, attempts to improve ceramics are still dominated by traditional "heat and beat" methods that parallel those developed earlier by physics-oriented metallurgists. However, after a few years during which momentum was building, interest in alternative, chemical methods for synthesis of ceramics surged in 1983. The idea, as explained by Donald Ulrich of the Air Force Office of Scientific Research, which has sponsored much of the research in this area, is to go back to "square one" in ceramics synthesis. Ceramists have little control over their starting material. Powders obtained by grinding solid material may be of nonuniform composition, size, and shape, for example. No matter how well conceived subsequent processing steps may be, the quality of the final ceramic is limited by what one starts with.



Air Force Office of Scientific Research

Sol-gel process

Changes in structure that occur during the transition from sol to gel to glass.

The hope is to control the structure of features in ceramic materials having characteristic length scales of 10 nanometers and up. The small length scale has given rise to the term ultrastructure processing. Particularly important are interfaces, such as the surfaces of pores and cracks and the grain boundaries between neighboring regions having different crystallographic orientations, because these are the weak spots where mechanical failures originate.

Researchers also want to be able to fabricate composite structures, such as the ceramic fiber reinforced glasses and metals that have been intensively studied for several years, with the same kind of precision control. In fact the natural world is filled with such composite structures, according to Ilhan Aksay of the University of Washington. An abalone shell, for example, consists of calcium carbonate whiskers less than 0.5 micrometer in diameter ordered in a protein matrix. Researchers would like to do as well with artificial structures.

The chemical technique that has attracted the most attention is sol-gel processing. The sol is a suspension of small particles (colloids) ranging in size from about 1 to 100 nanometers. On partial loss of the liquid phase, the sol increases in viscosity, eventually becoming rigid; that is, it becomes a gel. The gel is the starting material for subsequent processing stages in ceramic fabrication.

While the popularity of sol-gel processing for ceramics has skyrocketed in the last 3 years, according to statistics presented at the MRS Symposium by Peter Morgan of the Rockwell International Science Center, these techniques have previously been widely exploited by chemists working in other fields, such as catalysis. Moreover, Walter Klemperer of the University of Illinois, who presented the lead-off paper at the MRS symposium, told those attending that the idea is at least 140 years old. In 1846, the French chemist Jacques Ebelman reported the formation of a transparent solid that could be drawn into fibers, although it was not until the 1920's that the chemistry was understood. After the mixing of tetrachlorosilane ($SiCl_4$) and ethyl alcohol to form the alkoxide tetraethylorthosilicate [$Si(OC_2H_5)_4$] and subsequent sol-gel reactions, the solid that emerged was an inorganic polymer with a silicon-oxygen backbone, that is, a silica ceramic. Nowadays, most sol-gel research also involves metal oxide ceramics made from metal alkoxides, although nonoxide materials and other synthesis routes are increasingly being investigated, points out J. Jeffrey Brinker at Sandia National Laboratories.

Already, researchers can make ceramics with a wide variety of properties by sol-gel processing, although in almost all cases the economic utility of this approach is still an unanswered question. The work reported at the MRS symposium by Edward Pope of the University of California at Los Angeles (UCLA) shows what it is now possible to do with sol-gel processing. Pope, who works in J. D. Mackenzie's laboratory at UCLA, described several types of oxide-nonoxide ceramic composites with optical and mechanical properties not available in conventional materials. Materials processing begins with mixing water, ethyl alcohol, a catalyst, and tetraethylorthosilicate. Subsequent steps depend on what type of composite is to be prepared, but they all take place at much lower temperature than the usual glass- or ceramic-forming processes, potentially a considerable economic advantage.

> ***Attempts to improve ceramics are still dominated by traditional "heat and beat" methods.***

To make lightweight, transparent polymer-oxide composites with controllable indices of refraction, for example, the solution is cast in a mold and allowed to gel, which produces a transparent silica gel comprising a network of particles about 5 nanometers in diameter and pores between the particles about twice this size. After drying and heat-treatment steps, the porous gel is impregnated with monomers, which subsequently polymerize at room temperature in pores of the gel. The porosity can be controlled by the catalyst and by the temperature and time of the heat treatment. Polymers including polymethyl methacrylate and silicone and copolymers (polymer alloys) involving these and other polymers have been incorporated in this way. The polymer species and concentration determine the index of refraction.

One problem with ceramics made by the sol-gel process is that they are highly susceptible to cracking because of the large shrinkage (up to 85% in experiments at UCLA) that occurs during the drying and heat-treatment stages. However, it is possible to make large, crack-free solids by adding a particulate second phase to the initial solution. It turns out that the second phase reduces the shrinkage. After the usual mixing, casting, gelation, drying, and heat-treatment steps, one obtains a porous ceramic composite. Pope mentioned several second phases that had been successfully incorporated into silica gels by this means, including silicon carbide whiskers, alumina, and silicon nitride. A silica–silicon carbide composite exhibited a maximum shrinkage of 30% for heat-treatment temperatures up to 800°C, while others did less well.

Finally, Pope discussed the fabrication of so-called triphasic composites by the impregnation of liquid monomers into porous composites followed by room-temperature polymerization. One remarkable lightweight silica–silicon carbide–polymethyl methacrylate triphasic exhibited a metal-like maximum deformation (strain) of 13.5% before fracturing under compressive stress, had a resistance to abrasion almost as good as that of commercial silica glass, and had a maximum processing temperature of 60°C. Pope attributed the large deformation to the possible retardation of crack growth by the silicon carbide.

Eventually, researchers would like to control structure at the molecular level. At Illinois, Klemperer, Vera Mainz, and D. M. Millar are trying what they call the molecular building block approach to the synthesis of ceramic materials. The idea is to start with a molecule with a controllable composition and structure that is to be the colloid particle in the sol. Subsequent hydrolysis and condensation reactions leading to the gel are, it is hoped, gentle processes that do not disrupt the basic structure of the building block but only remove the unwanted organic groups and water molecules. The particular molecules being investigated are polysilicic acid ester monomers, such as $[Si_3O_2]$-$(OCH_3)_8$ and $[Si_8O_{12}](OCH_3)_8$. At the moment, the Illinois chemists have demonstrated the utility of nuclear magnetic resonance techniques to study the progress of the reactions but have yet to find the reaction conditions that will allow them to produce silica glass by the sol-gel route with these monomers.

All in all, these two examples give hardly more than a flavor of current activity. The MRS symposium alone had 117 oral and poster papers, up from about 50 at the previous "Better Ceramics Through Chemistry" session 2 years ago. Moreover, sol-gel processing is far from the whole story. Researchers are keenly interested in adapting other concepts from organic synthesis and polymer chemistry to the fabrication of inorganic ceramics, as well. Nonetheless, while the large number of American industrial participants (no papers were given by Japanese authors) suggests that companies are interested in the new ideas, most of the reports dealt with processing stages that occur well before the fabrication of a densified ceramic product, indicating a promising but as yet unproven contribution for chemistry in making better ceramics. ■

ARTHUR L. ROBINSON

ADDITIONAL READING

L. L. Hench and D. R. Ulrich, Eds., *Science of Ceramic Chemical Processing* (Wiley, New York, 1986).

S. J. Schneider, Ed., *A National Prospectus on the Future of the U.S. Advanced Ceramics Industry* (NBS Report IR 85–3240, National Bureau of Standards, Washington, DC, 1985).

E. P. Rothman, J. P. Clark, H. K. Bowen, "Ceramic turbocharger cost modeling and demand analysis," in preparation.

Briefing:

Planetary Rings May Not Be Forever

The more closely planetary scientists look at the rings circling the outer planets, the harder it is for them to imagine that the rings they see today are the same ones they would have seen 100 million years ago or will see even a few decades hence. The forces eroding the rings seem to be working too fast on some of them for such stasis. Rather than dating from the formation of the solar system 4.5 billion years ago, some rings may be young, formed by the violent destruction of a moon or the breakup of an earlier ring.

The latest indication of the possible mutability of planetary rings is reported in this issue of *Science* (p. 74) by Lyle Broadfoot of the University of Arizona and his colleagues on the ultraviolet spectrometer team of the Voyager 2 spacecraft. Their instrument focused on the uppermost reaches of the detectable Uranian atmosphere, including its emission of the mysterious electroglow that in pre-Voyager observations masqueraded as auroral emissions. The electroglow's source of energy is unknown, but in the course of driving the electroglow it also breaks down hydrogen molecules into hydrogen atoms that have enough energy to escape the atmosphere in large numbers. This atomic hydrogen boiling away from the planet joins an exceptionally dense extended hydrogen atmosphere bound to the planet that has a density of 100 to 1000 atoms per cubic centimeter at the distance of the Uranian ring system.

Particles orbiting through this extended atmosphere would not feel much of a breeze by terrestrial standards, but the resulting drag could pull any particles except large boulders into a slow spiral ending within a few billion years in incineration in the lower atmosphere, according to calculations by the ultraviolet spectrometer team. A 1-micrometer ring particle unconstrained by any other forces would survive just 100 to 1000 years. The plethora of dust rings and bands discovered in Voyager images suggests that gas is indeed dragging such particles across the system from the rings, where particle collisions presumably create them.

Larger particles, from centimeter- to meter-sized, would last 100,000 to a billion years, still far short of the age of the solar system. An unconstrained ring having particles all the same size and a mass as large as that of the epsilon ring, the most massive of the Uranian system, would last only 600 million years. In fact, the epsilon ring and probably the other nine narrow Uranian